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RUBBER CHEMISTY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published periodically under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important published papers on fundamental research, technical developments and chemical engineering problems relating to rubber or its allied substances.

Members of the American Chemical Society who are also paid members of the Rubber Division are entitled to receive this publication. Any other individual corporation or organization interested in rubber, though not a member of the American Chemical Society, is eligible to become an associate member of the Rubber Division upon payment of $6.00 annually and is thereby entitled to receive this publication.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pa., or Municipal University, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

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Minutes of the September Meeting at Swampscott, Mass.

The Rubber Division meeting was called to order by the Chairman, Harry L. Fisher, at the Preston Hotel, Swampscott, Mass., on September 11, at 2:00 P.M., with about 300 in attendance.

In the opening session the chairman appointed the following committees: *Resolution:* W. B. Wiegand, W. G. Nelson, E. H. Grafton. *Nominating Committee:* C. R. Boggs, L. B. Sebrell, D. F. Cranor, W. N. Jones, W. W. Evans. *Committee on Physical Testing:* W. A. Gibbons, Stanley Krall, W. W. Vogt, J. W. Schade, N. A. Shepard, A. A. Somerville, D. F. Cranor, E. R. Bridgwater, J. M. Bierer, W. L. Sturtevant. The program was carried out as printed.

At the time the Nominating Committee made their report they suggested that the retiring Chairman of the Division be made a member of the next year's Executive Committee. The Nominating Committee made its report and the election was held, resulting in the placing in office of the following officers for the year 1929: *Chairman*, A. H. Smith; *Vice Chairman*, Stanley Krall; *Secretary-Treasurer*, H. E. Simmons; *Executive Committee*, H. L. Fisher, E. R. Bridgwater, S. N. Cadwell, C. W. Sanderson, H. A. Winkelmann.

The Resolutions Committee submitted the following resolutions, which by vote were unanimously approved:

No. 1—*Resolved*, that the Rubber Division extend its appreciation and thanks for the constructive work done by the Physical Testing Committee and especially for the efficient services of its retiring chairman, J. E. Partenheimer.

No. 2—*Resolved*, that the Rubber Division extend its thanks to C. C. Davis for his unselfish assumption of the important but onerous duties of editor of RUBBER CHEMISTRY AND TECHNOLOGY and for the brilliant way in which he is discharging these duties.

No. 4—*Resolved*, that the Rubber Division convey its warmest thanks to the local Committee of the Northeastern Section for its fine hospitality, resulting in such excellent provisions and arrangements for the conduct of the meetings and also for the entertainment of its members, their wives, and their sweethearts.

J. E. Partenheimer, as chairman of the Committee on Physical Testing, made a Progress Report, and E. B. Spear, chairman of the Raw Rubber Specifications Committee, made a report for his Committee.

The Secretary-Treasurer's report showed that at the present time there are 353 members in the Division, 150 Associate Members, 6 Honorary Members, and 52 Subscribers to RUBBER CHEMISTRY AND TECHNOLOGY.

Financial Statement

In the bank April 16, 1928 (St. Louis Meeting)	$749.67	
Amount received from dues	801.00	$1550.67
Expenditures:		
Circular letter and envelopes	$36.25	
Telegrams, stamps, office supplies	11.62	
Postage, Insurance, Express	5.55	
Stenographic services	44.63	98.05
Balance in bank Sept. 12, 1928		$1452.62

H. E. SIMMONS, *Secretary-Treasurer.*

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the July 10 and 20, August 10 and 20, and September 10 and 20, 1928, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial and trade journals throughout the world.

Applied science in the service of the American rubber industry. F. KIRCHHOF. *Kautschuk* **1928,** 57–60; cf. *C. A.* **22,** 2077.—A further review and description of important features and developments. C. C. DAVIS

Progress in the chemistry, physics and technology of rubber and its most important compounding ingredients. F. KIRCHHOF. *Kautschuk* **1928,** 61–3.—Brief reviews in abstract form, with the original references. C. C. DAVIS

The development of the rubber industry in the last fifty years, with special reference to the German industry. FRIEDRICH DIESTELMEIER. *Kautschuk* **1928,** 68–73. C. C. DAVIS

Rubber research in the year 1927. MARIANNE PIECK. *Gummi-Ztg.* **42,** 1632–3, 1690–2, 1743–4(1928); cf. *C. A.* **21,** 2199.—Many original references accompany the review. C. C. DAVIS

Organic colors for use in rubber compounding. M. P. PARKER. *Rubber Age* (N. Y.) **23,** 135–6(1928).—A description of the properties and uses of certain red, yellow, orange, green, blue and brown org. coloring ingredients. C. C. DAVIS

Patent review. C. BÖHM. *Kautschuk* **1928,** 65–6; cf. *C. A.* **22,** 2077.—Numerous patents of different countries on the production of latex, raw rubber, mixing, vulcanization and the manuf. of rubber goods are itemized, with their essential features. C. C. DAVIS

Rubber compounding practice. WEBSTER NORRIS. *India Rubber World* **78,** No. 1, 59–61; No. 2, 55–7(1928); cf. *C. A.* **22,** 1251.—The properties and methods of *testing ZnO, TiO_2, lithopone, Sb reds, Fe oxides, HgS, ultramarine blue, Cr green and various yellow pigments* are reviewed. C. C. DAVIS

Open mill mixing vs. internal mixers. P. P. CRISP. *Rubber Age* (N. Y.) **23,**131–2(1928). C. C. DAVIS

Experiences with mixing-mill roll speeds, speed ratios and batch sizes. E. C. ZIMMERMAN. *Rubber Age* (N. Y.) **23,** 144–5(1928). C. C. DAVIS

Power variables in milling and mixing rubber. P. S. SHOAFF. *Rubber Age* (N. Y.) **23,** 142–4(1928). C. C. DAVIS

Design of properly cooled rubber machinery. A. P. LEWIS. *Rubber Age* (N. Y.) **22,** 533–4(1928). C. C. DAVIS

Factors in supply and use of cooling water (in the manufacture of rubber). P. S. SHOAFF. *Rubber Age* (N. Y.) **22,** 531–2(1928). C. C. DAVIS

Chilled iron rolls in the rubber industry. N. W. PICKERING. *Rubber Age* (N. Y.) **23,** 137–41(1928). C. C. DAVIS

Gutta-percha as a dielectric material. ST. REINER. *Kautschuk* **1928,** 55–6; cf. *C. A.* **21,** 1567, 3767.—A review of present developments. C. C. DAVIS

Rubber jar rings for preserving. H. SERGER. *Konservenindustrie* **1928,** 129; *Gummi-Ztg.* **42,** 1480–1(1928).—Specifications for the quality and behavior of rings are described. C. C. DAVIS

An experiment on heavy tapping on Tjiseroe Estate. Investigation of the rubber and some remarks on the composition of the latex. W. SPOON. *Arch. Rubbercultuur* **12,** 207–16(1928). (In English 217–9.)—Heavy tapping in the case cited resulted in a latex with low rubber content and rubber which vulcanized rapidly and had a low viscosity compared with rubber obtained under normal conditions on the same estate. C. C. DAVIS

Effect of heat on raw rubber. C. R. PARK, C. M. CARSON AND L. B. SEBRELL. *Ind. Eng. Chem.* **20,** 478–84(1928).—Various types of raw rubber were heated in steam

at 158° in the absence of air to det. the influence of such treatment on the plasticity and chem. properties before vulcanization and on the quality after vulcanization, with and without an accelerator. Under these conditions the plasticity, the acetone ext., the acid no. and the rate of vulcanization increased, while the total N decreased. An increase in acetone ext. may result from partial depolymerization of the rubber or from hydrolysis of proteins. An increase in acid no. probably results from hydrolysis of fatty acid esters and proteins. The total N decreases because of the evolution of volatile N compds. In comparative vulcanization tests before and after heat treatment, the rate of vulcanization was increased with some accelerators but not with others by preheating the rubber, and the stress-strain curve became more convex toward the strain axis, *i. e.*, a tendency toward softer products, a difference which persisted after aging. Preheating rubber did not impair the aging of its vulcanizates. To det. why heating rubber increases its rate of vulcanization, protein decompn. products were added to different mixts., and also the water ext. of heated rubber was analyzed. The most active products in mixts. contg. ordinary accelerators were the least complex compds., *e. g.*, glycine, whereas in unaccelerated mixts. those with a strongly basic group and no acid group were most active. The aq. ext. of acetone-extd. rubber contained no substance which reduced Fehling soln., no tannin and no free amines, but did contain saponin, proteins, alkaloids and other N bases. Fractionated products from the alc. extn. of rubber (previously extd. with acetone and water) were also tested. These compds., though not identified exactly, included a *compd.* of the approx. compn., $C_4H_8O_2N$, monoamino acids, diamino acids and dicarboxylic acids. The alc. ext. activated accelerated mixts. The results show that only the simplest amino acids have any effect in unaccelerated mixts., that amines and N bases activate accelerated mixts. and that alkaloids have certain accelerating and activating effects. All 3 types are probably present in rubber, and the alterations brought about by heating rubber are attributable at least in part to changes in these non-rubber components. C. C. D.

Experiments on stretching raw rubber. P. Rosbaud and E. Schmid. *Z. tech. Physik* **9**, 98–106(1928).—The stretching of raw rubber (smoked sheet) was examd. in a Schopper app. between 5 and 100 kg. stress and in a Polanyi wire-stretching app. The sheet thickness was 2.0 to 2.5 mm., the length of the exptl. strips 6 mm. From expts. on the influence of rate of stretching (0.025% per sec. up to 50% per sec.) on the stress-strain curve, it was found that the tensile strength increased from 12 to 317 g. per sq. mm., while max. elongation was influenced less (360 up to 1280%). One expt. in which stretching periods were alternated with rest periods of several hrs. (total duration of expt. 350 hrs.) proved that the rubber flows in the rest periods, and that with continued stretching small stresses of the order of 10 g. per sq. mm. are sufficient to bring about rupture. At temps. from —20° to +80°, the tensile strength decreases for rapid or slow stretching rapidly with increasing temp.: for a 14% per sec. rate, it drops from 3100 g. per sq. mm. (5900 at —185°) at —20° to 24 g. per sq. mm. at +80°. The max. elongation increases slightly with temp. (1000% to 2000% roughly); at very low temps. (liquid air) it is negligible, and at —80° it is about 50%. At the more elevated temps. especially from 60° on local contractions of the rubber occur, which on continued stretching spread all over the strip. Polanyi's observations of increased strength at —185° after preliminary stretching at a higher temp. were confirmed. The results are represented in a space diagram: tensile strength vs. rate of stretching vs. temp. B. J. C. van der Hoeven

"Normal" aging of compounded rubber. R. H. McKee and H. A. Depew. *Ind. Eng. Chem.* **20**, 484–91(1928).—Nine widely different types of cured rubber mixts. were aged for 4 yrs. (1) outdoors protected from direct light but subject to normal variation of temp. and humidity (—17.8 to 37.8° and 40–100%); (2) indoors in darkness (10–29.4° and 25–100% humidity); (3) in darkness in a continuous current of dried air, and (4) in darkness in a continuous current of humidified air. The mixts. stored in a damp atm. showed "softer" stress-strain curves than the same mixts. kept dry. Judged by tensile strength, overcured mixts. deteriorated more rapidly in a dry atm. than in a wet atm., whereas the reverse was true of undercured mixts. Judged by gain in wt., underground mixts. oxidized at about the same rate whether the atm. was wet or dry, whereas overcured mixts. oxidized more rapidly in a dry atm. than in a wet atm. The change in wt. of mixts. kept dry proved to be a good criterion of their deterioration, each 1% gain (based on the rubber) corresponding to a decrease of about 50% in reinforcing properties. The mixts. were then aged under strains of 50 and 20% outdoors in sunlight and indoors in darkness. In sunlight, overcured mixts. became surface-checked sooner than the corresponding undercured mixts., whereas in darkness the reverse was the case. The effect was, however, confined to the surface. Paraffin and Zn oxide retarded this action of light, and there is probably a close relation between the protection of paint and of rubber from deterioration by light. When the uncured

mixts. were stored, their rate of vulcanization became notably slower, perhaps because of oxidation of S to SO_2 and H_2SO_4. Some of the uncured mixts. became tacky. C. C. DAVIS

Diffusion experiments with rubber solutions. D. KRÜGER. *Gummi-Ztg.* **42**, 1471–4(1928).—Acetone extd. and unextd. samples of various rubbers and balata were swollen in solvents in darkness and with agitation, and were then centrifuged. With the exception of balata, soln. was practically complete. There was no change in viscosity after the solns. were kept for 2 weeks (cf. van Rossem, *Kolloidchem. Beih.* **10**, 83(1918)). *Diffusion coeffs. of rubber-hexane, rubber-Et_2O and rubber-C_6H_6* were detd. by the Oeholm method (*Z. phys. Chem.* **50**, 309(1905)) and the Scheffer-Kawalki tables (*Ann. Physik* [3], **52**, 185(1894)), 4 superimposed strata being measured. The results are tabulated in detail. The influence of temp. was very slight. Unlike the case of a chem. homogeneous substance with uniform particles, the diffusion const. of rubber increased from the bottom to the uppermost layer. Highly masticated rubber, in spite of its relatively concd. solns., showed smaller differences among the 4 strata than did unmilled rubber. The rubber content of the second layer deviated so much from the Fick law that the Scheffer-Kawalki tables were inapplicable. The variation of the diffusion coeff. with increasing concn. and with decreasing time of diffusion might have resulted from (1) a mixt. of chem. different substances of different mol. wt., not, however, by the resins, or (2) different degrees of aggregation of the same substance. The data obtained are not adequate for a mathematical analysis of the variations of the diffusion coeffs. There were indications that a readily diffusible component was distributed uniformly throughout the 4 strata, while a difficultly diffusible component remained for the most part in the lowest layer. The diffusion coeff. depends upon the concn., and furthermore different results were obtained depending upon whether the soln. was allowed to diffuse immediately after prepn. or was let stand. Diffusion coeffs. are therefore not characteristic consts. but mean values which depend upon the relative quantities of small and large particles in the individual layers. The nature of the solvent also influenced the coeff., probably because different liquids differ in their ability to disaggregate the rubber to simpler units. C. C. DAVIS

Tensile properties of soft rubber compounds at temperatures ranging from —70° to +147°. R. F. TENER, S. S. KINGSBURY AND W. L. HOLT. Bur. Standards, *Tech. Paper* No. **364**, 367–77(1928).—Elongation and tensile strength tests of 6 widely different types of cured rubber mixts. at 147°, 130°, 100°, 70°, 40°, 23°, 10°, —10°, —30°, —50°, —60° and —70° show that these properties vary greatly with variation in the temp. In all cases the elongation was a max. around 100° and diminished both above and below this range. From —50° down, it diminished very rapidly and at —70° the mixts. were rigid and inelastic. The tensile strengths were a max. at —70° and diminished continuously up to 147°, at which point there remained almost no strength. The various rubber mixts. behaved essentially in the same way and differences resulting from compounding ingredients were in degree rather than in kind. The results are shown graphically, including the stress-strain curves of the various mixts. The results are of great importance in connection with the design of products contg. rubber which are to be used under very cold or hot conditions. Cf. van Rossem and van der Weijden, *C. A.* **22**, 1059. C. C. DAVIS

Prevention of scorching of rubber mixtures during the mixing operation. WERNER ESCH. *Kautschuk* **1928**, 51–5.—PbO_2 is very effective in preventing the scorching of various types of rubber mixts. accelerated with tetramethylthiuram disulfide. About 0.25% (based on the rubber) gives good results. Pb oleate and golden Sb also have a favorable influence. Such addns. also reduce the tendency to scorch in mixts. accelerated otherwise, *e. g.*, by mercaptobenzothiazole and diphenylguanidine. C. C. D.

The absorption of hydrogen by rubber at elevated pressures and the behavior of the rubber after the pressure is lowered. G. TAMMANN AND K. BOCHOW. *Z. anorg. allgem. Chem.* **168**, 322–4(1928).—When rubber, Zn and dil. H_2SO_4 are subjected to high pressures, *e. g.*, 550 or 1150 kg. per sq. cm., the rubber becomes satd. with H, so much being absorbed that when the pressure is released the rubber is porous, and some time afterwards is still several times its original vol. C. C. DAVIS

Some features of sulfur in rubber manufacture. D. F. TWISS. *Trans. Inst. Rubber Industry* **3**, 386–400(1928).—A crit. review of the *properties of S* and *its use in rubber*, including the different *allotropic forms of S and their properties*, the *soly. of S in rubber*, "*blooming*," the *phys. effects on rubber induced by S*, and possible explanations of these effects. Influences which favor internal crystn. of S in rubber inhibit blooming and the latter may be minimized by (1) cool conditions during milling to prevent complete dissoln. of S, the undissolved particles acting as nuclei for internal crystn.; (2) not too fine S; (3) a high enough proportion of S to furnish a residue of undissolved S; (4) the addn. of a relatively insol. cryst. substance isomorphous with rhombic S to act

as permanent nuclei for crystn., *e. g.*, Se, and (5) the use of S flowers contg. insol. S. Measurements by various investigators of the *vapor pressure of S* from 125 to 225° do not agree closely. A vapor pressure-temp. curve constructed from calcns. based on the Ramsay and Young law and the vapor pressure of Hg gave results which agree satisfactorily with the best exptl. data and are continuous over the range of temp. From this curve and with the assumption that below 300° S vapor is octatomic, the max. wt. of S which can vaporize into a given vol. of gas at different temps. can be calcd. A crit. review of theories which assume that S_π or S_μ is the form which induces vulcanization shows that these theories are inadequate to explain the phenomena (cf. T., *C. A.* **11**, 2973; T. and Thomas, *C. A.* **15**, 1421), and new exptl. evidence is given to support this view. The earlier evidence in conjunction with the new expts. leads to certain important conclusions. S_μ is not appreciably more active than S_λ as a vulcanizing agent, and in the expts. described the rates of vulcanization were substantially the same. At ordinary vulcanization temps. S_μ changes very rapidly into S_λ. This tendency is so great that a mixt. of rubber, S_μ, ultra-accelerator and ZnO in a solvent forms a gel nearly as soon as a similar mixt. contg. S_λ in place of S_μ. The regularity of the increase in the rate of vulcanization with increase of temp. indicates that between 60° and 188° the increasing proportion of S_μ and S_π relative to S_λ has no marked accelerating action on the rate of vulcanization. This latter fact also controverts the theory of L. E. Weber (*Chemistry of Rubber Manufacture* p. 88) that only S_2 mols. bring about vulcanization. Evidence in general shows that whatever allotropic forms may be present in equil. in S under normal conditions, their activity toward rubber is practically the same. Evidence against the Dannenberg theory of vulcanization (cf. *C. A.* **21**, 3764) is very great and exptl. evidence is given to show that the theories of Dannenberg (*C. A.* **21**, 3764) and of Scholz (*C. A.* **21**, 2399) are extremely improbable. A mixt. of rubber with 10% S_μ shows no tendency to vulcanize. Vulcanization proceeds at substantially the same rate with S_λ and S_μ in a given mixt. S_μ cannot exist under vulcanizing conditions, for it is converted at 120° to S_λ and S_μ is not formed from S_λ to any appreciable degree below 170°. If combined S consisted solely of S_μ, treatment of vulcanized rubber with hot alkalies would remove combined S. The active, unstable form of S in the Peachy process is probably also formed when a rubber-S mixt. is exposed to sunlight or ultra-violet light, and this active form accounts for vulcanization under these conditions. Evidence is offered in support of the rubber sulfide reinforcement theory of T. (cf. *C. A.* **19**, 1964). C black changes the course of the stress-strain curve of a cured rubber-S mixt. in the same direction and in the same way as an increase in the state of cure, but a greater change can be brought about by C black than by longer vulcanization without an extreme overcure. In this connection a comparison of stress-strain curves of a rubber-S mixt. contg. C black and the same mixt. without C black but cured to higher states indicates that an ingredient like C black alters the phys. condition of the rubber in the same way as does further vulcanization but to a greater extent than is possible without undesirable effects. Therefore C black reinforces in the same manner as the curing process within a certain range of cure. Expts. by Bierer and Davis (*C. A.* **20**, 2092) which showed that the proper use of Se improves the resistance to abrasion of rubber mixts. contg. C black could not be confirmed. A general discussion follows the paper. C. C. DAVIS

Specifications for the construction of rubber goods and service requirements. WERNER ESCH. *Kautschuk* **1927**, 75–83; cf. Bierer and Davis, *C. A.* **22**, 883.—A discussion of various aspects of the subject. Comparative tests are tabulated of the *resistance to abrasion* on 2 different abrasion machines (N. J. Zinc Co. and B. F. Goodrich Co.) *of mixts. contg. C black with and without Se.* The resistance to abrasion depended upon the quantity of accelerator and of S, upon the presence or absence of Se and upon the state of cure. Near the optimum cure the 2 methods gave concordant results, but when mixts. were overcured, or undercured discordant results between the 2 methods were obtained. Se increased notably the resistance to abrasion (cf. Bierer and Davis, *C. A.* **20**, 2092; Twiss, *Trans. Inst. Rubber Industry* **3**, 386(1928)) and this superiority of the mixts. contg. Se was still manifest after aging in air at 70°. The improvement through Se illustrates the importance of non-rubber components in detg. the quality of rubber goods and the fallacy of specifying the chem. compn. of rubber goods as a criterion of quality. In further abrasion tests, mixts. in which rubber was partially replaced by a greater proportion of *reclaim* resisted abrasion better than the corresponding mixts. contg. no reclaim, and the addn. of Se increased the resistance still more. Other data show the quality of mixts. suitable for soles and the *superiority of C black over ZnO* in mixts. designed to resist abrasion. C. C. DAVIS

Aldol-α-naphthylamine. H. KLOPSTOCK. *Kautschuk* **1928**, 64.—Polemical (cf. Esch, *C. A.* **22**, 2078). C. C. DAVIS

Aldol-α-naphthylamine. WERNER ESCH. *Kautschuk* **1928**, 64.—A reply (cf. preceding abstr.) C. C. DAVIS

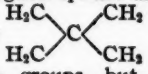
Recent scientific advances in connection with guayule. DAVID SPENCE. *Rubber Age* (N. Y.) **23**, 133–4(1928); cf. *C. A.* **20**, 3841; **22**, 333.—Further biochem. and chem. research on guayule is described. Most important is the discovery that rubber in guayule shrub does not exist in the cells in the form in which it is recovered but is present chiefly as a *colloidal suspension in the plant juices*. Within the cells the suspended globules are in rapid Brownian movement and their agglomeration and subsequent coagulation by ordinary reagents can be followed microscopically. The shrub contains about 10% water-sol. substances (tannins, carbohydrates, N substances, etc.), 10–15% substances sol. in water after hydrolysis (pectins, proteins, etc.), besides cellulose and resins. By fermentation of the carbohydrates into sugars, org. acids and CO_2 and by putrefactive decompn. of the protein, the acetone ext. of guayule rubber can be reduced 60–70% and the vulcanizing properties improved. Only a small part of the acetone-sol. substances is resinous, and by retting the shrub, the acetone ext. can be reduced from 25–30% to 9–10%, with consequent improvement in properties when vulcanized. The com. product is termed *Ampar rubber*. C. C. DAVIS

X-ray investigations of rubber and related substances. P. ROSBAUD AND E. A. HAUSER *Z. Elektrochem. angew. physik. Chem.* **33**, 511–13(1927).—This is a recapitulation of results obtained by this method. "Frozen" rubber, even unstretched, shows distinct Debye-Sherrer rings, which disappear when the rubber is thawed. When stretched, it gives a point diagram. Balata and gutta percha are very similar to frozen rubber. At higher temps. they can be stretched and then give typical fiber diagrams of identical character. At high tension, a point diagram is produced, giving a characteristic interval of 9.35 A. U. in agreement with Clark's (*C. A.* **20**, 3837) value of *c*. His values $a = b = 5.40$ A. U. are not substantiated; but the unit cell is certainly small, contg. between 2 and 8 mols. Racked rubber is analogous to stretched balata and gutta percha, giving a very distinct x-ray diagram and indicating extensive orientation of the particles. Rubber fractionated by Pummerer's method shows clear point diagrams in the sol, gel and total fractions, whether stretched or cold-vulcanized. A. W. KENNEY

Rubber inventions and processes. ANON. *Bull. Rubber Growers' Assoc.* **10**, 237–9(1928).—Seven British patents are described. C. C. DAVIS

The Italian rubber industry. H. B. NEWMAN. *Rubber Age* (N. Y.) **23**, 203–4 (1928).—A survey of present developments. C. C. DAVIS

Use of "Moac" in the rubber industry. RUDOLF DITMAR. *Caoutchouc & gutta-percha* **25**, 13,968(1928).—"Moac" is a very finely divided form of mica which when used as a dusting agent gives a silky luster resembling that of Al powder. Because of its ability to increase the dielec. const. of rubber when used as a filler, it is also useful in rubber goods for elec. use. When the surface of rubber is swollen slightly with C_6H_6 and "Moac" is rubbed in, the rubber is protected from subsequent oxidation. C. C. DAVIS

Earlier observations and new hypotheses on (the structure of) rubber. J. DUGUÉ. *Rev. gén. caoutchouc* **1928**, No. 40, 3–9.—A review of various aspects of the subject is followed by the development of a new hypothesis to explain the *tackiness, plasticity, elasticity, hysteresis* and *structure of raw rubber*. This is based on chem. activity resulting from a peculiar spatial arrangement of the atoms in the rubber mol., a unique structure which is most comprehensible by reference to the original spatial diagrams. There are no double bonds and the mols. are constructed of  nuclei. Within the mols. these nuclei are united through the CH_2 groups, but on the extremities or on the exterior (depending on the spatial structure), certain CH_2 groups are unsatd. and exert forces of attraction which, in the presence of other similar groups, are manifest as tackiness. With this as a basis, the other characteristic properties are explained. C. C. DAVIS

Investigations of sodium fluosilicate. L. R. VAN DILLEN, C. KNAUS, G. M. KRAAY AND R. RIEBL. *Arch. Rubbercultuur* **12**, 61–125(1928). (In shorter form in English 126–54.)—The investigations include a study of the *most economic method of coagulation with Na_2SiF_6*, the *corroding action of Na_2SiF_6 on Al*, the *relation between the p_H value and coagulation*, the *influence of Na_2SiF_6 on the phys. properties of rubber*, and the *influence of Na_2SiF_6 on the tendency of rubber to become moldy*. Though too close a comparison between the small and large scale expts. is not justified, owing to certain variables in the methods and technic on different plantations where the expts. were made, the large no. of expts. warrant certain general conclusions. Coagulation with Na_2SiF_6 of latex contg. more than 15% dry rubber was nearly always incomplete, the serum

remaining milky, and contg. rubber even on standing 24 hrs. after a large dose of Na_2SiF_6. Latex with only 12% rubber was completely coagulated in 24 hrs. and sometimes in a shorter time. In all expts. 8–10 g. of Na_2SiF_6 per kg. of dry rubber were required for the satisfactory coagulation of latex contg. 12% rubber, and even then the serum was sometimes milky. In general the coagulating power of Na_2SiF_6 was very sensitive to small variations in the state or compn. of the latex, *e. g.*, its p_H value. Expts. showed that Na_2SiF_6 solns. have an acid reaction (cf. *J. prakt. Chem.* **32**, 300 (1885)) because of hydrolysis, *e. g.*, 0.1 and 0.5% aq. solns. showed p_H values of 3.1 and 3.4, resp., at 30.5°. The clearness of the serum and its p_H value were closely related, the most complete coagulation, without loss of rubber, occurring in the range p_H 4.4–4.5. This range is most readily controlled by diln. of the latex. This acid reaction causes aq. Na_2SiF_6 to attack Al, so that Al equipment is impracticable. Comparative tests of the loss of wt. of Al in different solns. for 24 hrs. showed the following % losses: water, 0.0; 0.5% Na_2SiF_6, 0.2; 0.1% Na_2SiF_6, 4.6; Na_2SiF_6 serum, —0.9; 5% $MgSiF_6$, 0.1; 0.1% $MgSiF_6$, 2.8; 2.5% HCO_2H, 0.2; HCO_2H serum, 0.0; 5% AcOH, 0.1; 5% $NaHSO_3$, 2.6. The gain in wt. with Na_2SiF_6 serum was due to a deposit on the Al. This Na_2SiF_6 serum subsequently ppts. a white flaky *substance* contg. 43% ash. The variable losses with different concns. of Na_2SiF_6 and of $MgSiF_6$ depend upon the deposition of products on the Al, which temporarily protect the latter from further attack. The influence of Na_2SiF_6 on the formation of air bubbles remained unsettled, though evidence indicated that it tends to diminish bubble formation. Aside from a tendency to retard the rate of vulcanization, Na_2SiF_6 had no material effect on the phys. properties of rubber. An advantage of Na_2SiF_6 was found to be its bleaching action, as a result of which only about 0.5 the usual quantity of $NaHSO_3$ need be used for producing pale crepe. On the other hand Na_2SiF_6 caused a temporary stickiness during creping of the coagulum, but this was no longer manifest in the dried crepe. Used as a coagulant alone or in combination with acid, Na_2SiF_6 had no influence on the tendency of rubber to become moldy, whereas immersion of sheeted rubber for a short time in concd. aq. Na_2SiF_6 greatly diminished any subsequent growth of mold. Certain evidence, however, showed that this immersion increased the formation of air bubbles, in which case the economy of Na_2SiF_6 as a disinfectant is seriously impaired. The advantages of Na_2SiF_6 as a coagulant rest on its use in the solid form, its tendency to reduce air bubbles, and its economy compared with HCO_2H; its disadvantages are the necessary diln. of the latex and the consequent larger app., and its corrosive action on Al app. Though coagulation by Na_2SiF_6 is cheaper than by HCO_2H, its general use is not recommended at present, and only where abnormal air bubble formation is encountered is it recommended as a coagulant, and only in cases of serious moldiness is immersion in aq. Na_2SiF_6 recommended. C. C. Davis

The behavior of Prussian blue and some other ferrocyanides in rubber. J. R. Scott. *India Rubber J.* **75**, 549–50(1928).—The investigation includes (I) the effect of Prussian blue (I), Turnbull's blue (II), $Pb_2Fe(CN)_6$ (III), and $Zn_2Fe(CN)_6$ (IV) on uncured rubber; (2) the behavior of I and II during mixing and (3) the effect of I, II, III and IV on the phys. properties of cured rubber. The particle size of III and of IV were 1.3 and 3.5μ, resp. I and II had a particle size of approx. 0.25μ, but whereas I dispersed easily and completely, II dispersed only with difficulty and incompletely, the reverse of their behavior in water. Their dispersion was not influenced by the presence of S in the rubber. However, rubber contg. I but no S became soft and sticky when milled, whereas rubber-I-S mixts. were too tough and elastic to sheet. The latter effect was not a result of incipient vulcanization, for analysis showed the absence of combined S. When stored for a few weeks or heated to 90° for 1 hr., rubber-I mixts. became very soft and fluid, while rubber-I-S mixts. became tougher and more elastic, changes probably identical with those occurring during mixing. When immersed in C_6H_6, rubber-III and rubber-IV mixts. became viscous and diffused slowly, and in general they behaved like masticated raw rubber. On the other hand, rubber-I and rubber-II mixts. retained their structure, swelled at a continuously diminishing rate and in general behaved like slightly vulcanized rubber or rubber-C black mixts. Rubber-I, rubber-II, rubber-III and rubber-IV mixts. with and without S, and in turn with and without quinol (as antioxidant) were stored in air and *in vacuo*. In air and without S or antioxidant, I and II accelerated oxidation so that the rubber-I and rubber-II mixts. became tacky and resinous, whereas III and IV were without influence, showing that ferrocyanides as a class do not accelerate the oxidation of rubber. The oxidation induced by I and by II is greatly retarded, though not inhibited, by S and by an antioxidant. Rubber-I and rubber-II mixts. appeared black by reflected light, and the n values of I and II were found to be 1.55 and 1.54, resp., the same as rubber, so that the mixts. appeared black for this reason. With the addn. of a white pigment, however, the mixts. became blue. On hot vulcanization, rubber-S mixts. contg. I and II became

green and brown-green, resp., as a result of decompn. of I and II by heat, rubber, rubber resin and S. I and II did not have a reinforcing effect in keeping with their fineness, but no evidence could be found that this was a result of agglomeration. C. C. D.

The rotatory power and the melting point of the resins in gutta-percha, balata and allied gums. S. MINATOYA AND H. KANEKO. *Researches Electrotech. Lab.*, Tokyo, Japan, No. **223,** 18 pp. (1928).—The authors collected 26 kinds of gutta-percha, 8 kinds of balata and 3 varieties of allied gums, such as African flake, jelutong and reboiled jelutong. Their resinous substances were sepd. into the following 3 groups by means of soly. differences in abs. alc.: (1) fluavil, (2) spherical alban, (3) needle alban. The rotatory power and the m. p. of these 3 groups of resins in all the samples were detd. The results of the expts. are summarized as follows. The m. ps. of fluavils of gutta-percha lie between 37° and 90° and they can never be found in liquid form at room temp. Fluavils of balata, on the other hand, are always obtained in liquid form at room temp. with only 1 exception, the fluavil of F. A. Q. Iquitos reboiled block balata has a m. p. of 43°. The m. ps. of spherical albans of gutta-percha lie between 54° and 200°. The needle alban content in gutta-percha is generally so small that the m. p. detn. is difficult, but 2 kinds of gutta-percha, *i. e.*, Kamper white and Siam white, contain just enough of the needle alban to measure the m. ps., which were 192° for Kamper white and 90–96° for Siam white. Generally speaking, the m. ps. of needle albans are higher than those of spherical albans. The quantity of spherical and needle albans in balata is insufficient to det. the m. p. The $[\alpha]$ values of fluavils of gutta-percha lie between 32.23° and 58.33°, with 2 exceptions, Bagen Seen and Pokan Seen. The $[\alpha]$ values of the resins of the latter 2 kinds are very low, like with those of balata; *i. e.*, 21.66° for Bagan Seen and 18.00° for Pokan Seen. The $[\alpha]$ values of fluavils of balata, however, are generally low and lie between 13.83° and 37.33°. The $[\alpha]$ values of spherical albans of gutta-percha lie between 39.20° and 56.75°, while those of balata lie between 20.00° and 35.00°. The needle albans of gutta-percha and balata are not only insufficient in quantity to det. the specific rotation, but are difficult to dissolve in solvents, such as C_6H_6, for the purpose of measuring optical rotation. W. OGAWA

Puncture proofing pneumatic tires. CHAS. E. MULLIN. *Textile Recorder* **45,** No. 538, 65(1928).—A discussion of the products offered and the results obtained. CHAS. E. MULLIN

Automatic regulator for vulcanizers. ANON. *Engineering* **125,** 406(1928).—The app. which is described and illustrated (Drayton Regulator and Instrument Co., W. Drayton, England) automatically controls the rate of increase of temp. to a max., maintains the temp. const. at this max. point for the desired period of time and at the termination of the cure shuts off the steam supply, signalling the completion of the operation. C. C. DAVIS

Studies of the aging of vulcanized rubber. IV. Relation between wave length of light and the deterioration of vulcanized rubber. TAKEJI YAMAZAKI. *J. Soc. Chem. Ind. Japan* **30,** 804–13(1927).—Samples of vulcanized rubber were exposed to sunlight filtered through 1 of 4 glass plates, which were transparent down to 2900 A. U., 3130 A. U., 3300 A. U. and 4360 A. U., resp. Since heating of the sample by the light was unavoidable, the effect of heating alone was examd. in control expts., in which the sample was kept at 70–71° for 150 hrs. in darkness. The color of the rubber became darker by mere heating, but when the rubber was exposed to sunlight at 60–70°, the change in color was far more remarkable. The higher the degree of vulcanization, the greater was the change in color. Moreover, the rubber was hardened by the action of light. The shorter the wave length of the light and the higher the temp., the sooner did hardening occur. The action of light of 4300 A. U. was very weak, except for over-vulcanized rubber, which was noticeably hardened even by light of longer wave length. The acetone ext. increased with the time of exposure, the rate of increase being less when light of longer wave length was used. In some cases, the acetone ext. reached a max. and then decreased. It was considered that increase in acetone ext. was due principally to the oxidation of the rubber, and that the decrease in acetone ext. by the further exposure was due to a change in part of the oxidized products into substances insol. in acetone. A remarkable decrease in free S by the action of light and heat was also noticed. Y. NAGAI

The use of the analytical quartz lamp in the rubber laboratory. F. KIRCHHOF. *India Rubber J.* **75,** 791–3(1928).—See *C. A.* **22,** 2291. C. C. DAVIS

The distribution of compounding ingredients in rubber mixings. ST. REINER. *India Rubber J.* **75,** 795–6(1928).—See *C. A.* **22,** 2290. C. C. DAVIS

New rubber compression testing machine. C. L. HIPPENSTEEL. *Bell Labs. Record* **5,** 153–5(1928).—A new type of machine of improved mech. construction has been developed for use in the compression testal ready described (*C. A.* **20,** 1921). C. C. DAVIS

The resistance to extension of vulcanized rubber. II. R. ARIANO. *India Rubber J.* **75,** 759–61(1928); cf. *C. A.* **20,** 3362.—An English version of *C. A.* **22,** 2081. C. C. DAVIS

Homogeneous rubber and the idea of an elastic molecule. HEINRICH FEUCHTER. *Kautschuk* **1928,** 103–6.—An analogy is drawn between the structure and properties of racked rubber and of liquid crystals, which are known to be bundles of long mols. in parallel orientation. F. has assigned a melting temp. to racked rubber in the same sense that there are definite melting temps. for liquid crystals. There is a limit or optimum length of mol. for the formation of liquid crystals. But there may be endless mols. or chains in rubber and in other substances subject to polymerization. These may account for the similarities with liquid crystals, and also the differences such as plasticity and the absence of x-ray interferences for liquid crystals as compared with the definite fiber patterns for racked rubber. G. L. CLARK

Plasticity and elasticity of rubber. A. VAN ROSSEM AND H. VAN DER MEIJDEN. *Congrès international pour l'essai des matériaux* (Amsterdam) Sept. 12–17, 1927 (preprint), 8 pp.—The compression method was chosen for measuring the plasticity of uncured and cured rubber, but the Williams app. (*C. A.* **18,** 1763), was not used, because it does not measure plasticity. Instead of maintaining a const. total pressure over an increasing area, a const. pressure per unit area was used, which was readily accomplished by compressing the rubber on a raised circular plate of 1 sq. cm. area. If deformation under stress or compression is not permanent, a substance is either viscous or elastic, and therefore it is of great importance in detg. plasticity to measure not only the decrease in thickness but also the recovery and its rate. Three properties may be distinguished during deformation under shearing stress: (1) *plasticity, i. e.,* nstantaneous deformation and instantaneous recovery; (2) *plastic flow, i. e.,* no recovery after removal of stress, and (3) *pseudo-plastic flow, i. e.,* slow recovery (elastic after-effect) after removal of stress. In the expts. described, all these properties were investigated. Masticated crepe was maintained under pressure at 16°, 30°, 45°, 50°, 60° and 70° and the rate of deformation and the rate and extent of recovery after release were detd. The higher the temp., the softer was the rubber, judged by the extent of compression. At 16° a small elastic recovery was followed by a large elastic after-effect, with ultimate complete recovery. At 30° complete recovery took place, but more slowly. At 45° there was only partial recovery, and therefore at this temp. the masticated rubber was partly plastic. At 60° the plasticity became greater, and at 70° the rubber was almost completely plastic, the elastic after-effect being very small. The results show that compression-time curves are misleading, since masticated rubber at 16° is not plastic but shows pseudo-plastic flow with an elastic after-effect, whereas at 70° it is truly plastic. Vulcanized rubber-S (92.5–7.5) mixts. in different states of cure were then tested in a similar way, the rate of compression and recovery being measured at 18°, 100°, 130° and 147°. At 18° and after short cures, there was elastic recovery and elastic after-effect but no evidence of plasticity. With increase of cure, the elastic recovery increased rapidly so that after long cures it became the only effect. At 100° and short cures, there was elastic recovery, as well as some elastic after-effect and plasticity. The last 2 properties became relatively smaller with increase in time of cure until at long cures only elastic recovery was manifest. At 130° the phenomena were much the same as at 100°, with relatively more elastic after-effect. At 147° and short cures, the elastic recovery and after-effect were relatively less and the plasticity was greater. With increase in time of cure the elastic recovery increased, the elastic after-effect decreased and the plasticity decreased slowly, the latter so slowly that even after the longest cure it still played an important part in the properties. Cured rubber is therefore plastic to a considerable degree. When undercured, the plasticity is evident even at 100°, but when cured for longer times it shows considerable plasticity only at 147°. The results are given in detail in tabular and graphical form. C. C. DAVIS

An explanation of some of the difficulties in abrasion testing of rubber. HARLAN A. DEPEW. *Trans. Am. Soc. for Testing Materials,* Preprint No. **98,** 9 pp. (June, 1928).—Resistance to abrasion is not a fundamental property of vulcanized rubber, but is the resultant effect of resistance to cutting and resistance to tearing. The relative importance of these 2 component effects varies under different conditions of wear, and therefore an abrasion test can duplicate any particular condition of wear only if the cutting and the tearing factors are balanced in the same proportion as in the actual conditions of wear. This means a discontinuance of present abrasion tests and the development of a test for detg. resistance to cutting and to tearing where the proportional effect of these 2 actions can be controlled. This conclusion is based on expts. with different types of mixts. in different states of cure, abrasion being obtained on the original N. J. Zinc Co. app. and on a modified form in which wear was made inter-

mittent by continual lifting and rebound of the rubber from the track. The first type is largely a cutting test, whereas in the second type tearing is accentuated and cutting is minimized, the latter type more nearly simulating the effect on a tire. On the first type, the resistance to abrasion increases with the time of vulcanization, whereas on the second type the resistance is a max. at about the same cure at which the tensile strength is a max. Most abrasion machines accentuate the tearing effect, so that only the second type of app. is comparable with many conditions encountered in actual wear. C. C. DAVIS

Further experiments on the influence of fatty acids on vulcanization. G. STAFFORD WHITBY AND BURKE A. EVANS. *J. Soc. Chem. Ind.* **47**, 122–6T(1928); cf. W. and Greenberg, *C. A.* **21**, 341.—The conclusion of Martin and Davey that with a sufficiently high proportion of ZnO, accelerators are activated equally well either in the presence or absence of resin acids (cf. *C. A.* **17**, 2203; **19**, 3037) is true only of certain accelerators. Expts. show that with other accelerators, fatty acids have an activating effect even with a high proportion of ZnO. The expts. were carried out by curing resin-free rubber (acid no. of 20) with mercaptobenzothiazole (**I**), anhydroacetaldehydeaniline (**II**), "808" (**III**) and hexamethylenetetramine (**IV**), with different proportions of ZnO and with and without the addn. of different proportions of stearic, oleic or linoleic acid. With **I**, the addn. of an org. acid was necessary to effect vulcanization, regardless of the proportion of ZnO. Stearic acid had the greatest activating effect, oleic acid a weaker effect and linoleic acid the weakest effect. The *rate of vulcanization* increases with increase in the acid content, and the best results were obtained with a proportion of acid higher than that normally present in crepe or sheet, so that in general it should be advantageous to add stearic acid or its like to mixts. accelerated by **I**. The addn. of stearic acid to mixts. accelerated by **II**, **III** or **IV** also increased the rate of vulcanization, regardless of the proportion of ZnO, though not nearly so much as with **I**. The readiness with which *stearic acid and ZnO react* is shown by expts. in which stearic acid (1.5 g.) and ZnO (2.5 g.) in toluene (100 cc.) were (1) shaken 20 min. at room temp. and (2) boiled 40 min.,15% and 96%, resp. of the stearic acid reacting. Also in *India Rubber J.* **75**, 872–5(1928). C. C. DAVIS

Important shortening in the time of cure of dipped goods in sulfur chloride vapor. RUDOLF DITMAR AND GUSTAV BALOG. *India Rubber J.* **75**, 911(1928).—An English version of *C. A.* **22**, 1060. C. C. DAVIS

The vulcanized racking of broken rubber. HEINRICH FEUCHTER. *Kautschuk* **1928**, 48–51.—While racking is easily demonstrated with raw rubber it is very difficult with vulcanized. The action of heat upon the vulcanized racking of broken rubber (calendering) is the opposite of unvulcanized racking. Specimens 50 × 50 mm. of calender-racked vulcanized rubber were used. There was no sensible release of tension in the sense of an anisotropic elastic change in form (longitudinal or direction of calendering as compared with transverse) up to 100°. Thus vulcanized racking is thermoelastically form-conservative. The swelling is anisotropic: in 30 min. at 20° in benzine the dimensions increased 30%, longitudinal, and 104% transverse. Upon deswelling, the original dimensions are restored. The racking tension of vulcanized racking is reversibly removed by swelling, the *swelling defect*, is calcd. and plotted as a function of temp., decreasing with increase in temp. G. L. CLARK

Racking and restoration of unbroken rubber. HEINRICH FEUCHTER. *Kautschuk* **1928**, 8–12, 28–30; cf. *C. A.* **21**, 1898, 1902, 1903, 3487.—The phenomenon of racking is of the greatest importance both theoretically and practically, since the most essential structural elements of animal and plant tissues are similarly fibered. Methods of racking are reviewed. A small strip of rubber (best *Hevea* sheet) is grasped at the ends with both hands, and as quickly as possible stretched almost to the breaking point. After this max. adiabatic extension, the warm strip is cooled for a min. while held under tension. Upon release there is only a slight contraction, and a tough fiber is obtained. For racking at higher temps. the strip is immersed in warm water for 1 min., removed and instantly stretched. The following are representative data:

Racking in %	500	600	750	1000	2000	4000	10,000
Original cross section	2 × 2	2 × 2	2 × 2	2 × 2	2 × 2	2 × 4	2½ × 5
Original length	12	13	13	10	5	2.5	1
Racked length	72	91	110.5	110	105	103	101
No. of rackings	1	1	1	1	4	12	50
Preheating in H_2O	...	30°	50°	80°	80°	90°	90°

The breaking strength shows a max. of 130 kg. at 500% racking, and a min. elasticity at the same point on curves which do not include all of the tabulated data. Tables present also the time function of thermal release from racking, *e. g.*, the % release

at 95° for racking of 2000% is 1840% after 1 sec., 1900 after 1 min. and 1920 after 10 min. Next the heat function of thermal racking release is illustrated in S-shaped melt-lines (temp. *vs.* % residual set after racking release), *e. g.*, a piece racked 10,000% with a length of 10.1 cm. had the following lengths and % set: 20°, 10.1, 10,000%; 30°, 9, 8900%; 40°, 4.1, 4000%; 50°, 1.4, 1300%; 70°, 1.15, 1050%. With 500% racking at 20°. the breaking strength is 790 kg. per sq. cm. and the elongation at breaking is 60%, while at 30° the vastly different values are 125 and 540, resp.; at 95° 40 and 630. The crit. point for 4000% racking is at 40°, changing from 910 and 20 at 20° to 300 and 260. Data on the racking and relaxation of rubber D (diffusion-rubber) are presented. The melt line is much steeper than for crepe rubber, since by a change from 25° to 30° as the temp. of racking release, the % of residual set falls from 1000% to 5%. Conclusion: The racking of rubber is a function of the presence of the more sol. rubber D, which is the carrier of the elastic properties of raw rubber. The elasticity cannot be ascribed to mols. or aggregates of pure compds. or to the simple unit cell detd. by x-rays, but to a particle which embodies the necessary properties. In the colloidal micelle, a higher phys., chem. and thermodynamic entity, in which all parts are harmoniously bound, is to be found the source of elasticity. G. L. CLARK

The swelling of rubber. A contribution to the knowledge of swelling phenomena. P. STAMBERGER. *Rubber Age* (*N. Y.*) **23**, 321–2(1928).—An English version of *C. A.* **22**, 2078. C. C. DAVIS

Diffusion of oxygen through rubber. S. E. HILL. *India Rubber J.* **75**, 710(1928).—See *C. A.* **22**, 2091. C. C. DAVIS

The thermal and calorific values of rubber and rubber-like substances. M. LE BLANC AND M. KRÖGER. Univ. Leipzig. *Z. Elektrochem.* **34**, 241–4(1928); cf. *C. A.* **20**, 2431.—As a means toward the ultimate explanation of mol. phenomena such as polymerization, the absorption of heat as a function of temp. was measured in rubber under various conditions of rest and stress. Measurements of the sp. heat of rubber, stretched and unstretched, heated and not heated, vulcanized and unvulcanized, showed that in general the sp. heat increases with the temp. (—80° to 40°). There were certain irregularities noted, but these were not sufficient to render doubtful the conclusion cited. Max. points, *e. g.*, in the sp. heat-temp. curves, occurred close to the temp. of hardening and loss of elastic properties (in the range of —40°). C. C. DAVIS

The rubber fiber and the cellulose fiber. HEINRICH FEUCHTER. *Kautschuk* **1928**, 73–5.—To account for the properties of rubber for which simple theories of valence and at.-mol. ideas are inadequate, F. has proposed the principle of shell-aggregates and shell-crystn. with irrational indices—a crystal system with distorted space lattice arrangement. The elastic property of racking vulcanized rubber is compared with the optical properties of nitrocellulose (Ambronn). An analogy is estd., since in both cases a chem. action (vulcanizing with S, and nitrating, resp.) upon a fiber leaves intact an individual group or crystallite, whose disperse cryst. property is estd. as the elementary particle of an elastic colloidal aggregate. G. L. CLARK

The coloring of cold-cured rubber. W. E. SANDERSON. *J. Soc. Dyers Colourists* **44**, 137–42(1928).—The use of org. coloring substances in rubber goods cured with S_2Cl_2 is surveyed in a concise yet comprehensive manner, with the inclusion of formulas and details of processes used in the best modern practice. L. W. RIGGS

Degree of fineness and reinforcing power of rubber fillers. WERNER ESCH. *Gummi-Ztg.* **42**, 1921(1928).—The relation between the apparent d. and the true d. as a criterion of fineness, a concept already developed by E. long ago, is discussed. C. C. DAVIS

Studies on the aging of vulcanized rubber. V. Action of sunlight and heat on the mechanical properties of vulcanized rubber. TAKEJI YAMAZAKI. *J. Soc. Chem. Ind.* (*Japan*) **31**, 233–42(1928); Suppl. binding, 65–6. (In English.)—Five series were prepd. from the same mixt. of 92.5% rubber and 7.5% S by vulcanization at the same temp. for 5 different periods of time (60–180 min.). They were then exposed to bright sunlight in summer at room temp., and in winter at room temp., in early spring at 60–64° in an air oven and in darkness in a Geer oven. The time of exposure varied from 8 to 64 hrs. After treatment, they were tested for stress at 500% elongation, tensile strength and ultimate elongation, and in some cases the free S and acetone ext. were detd. Some test pieces were made especially thick, and slices were cut after exposure from outer and inner layers and were tested. The time of vulcanization had a remarkable effect on the aging properties. The deterioration due to sunlight was great even in winter and was very marked in spring at 60°. The acetone-sol. components increased during aging and the free S decreased. The outer layers of the test pieces exposed to sunlight were brittle and non-elastic, but the inner layers were in fairly good condition. The test pieces subjected to the Geer test showed only small differences between the outer and inner layers. For detg. the degree of deterioration,

mech. tests are quicker and more reliable than chem. tests, and in aging tests the influences of light must be taken into account. **VI. Action of sunlight filtered through colored glass on the mechanical properties of vulcanized rubber.** *Ibid* 243–57; Suppl. binding, 66–7. (In English.)—The test pieces were prepd. in the same way as in the preceding paper. The sunlight was filtered through one of 2 colored glass filters, (1) transparent down to 3300 A. U. and (2) down to 4360 A. U. The samples were exposed to the filtered light at 40° or 65° for various lengths of time and from 8 to 256 hrs. After treatment, they were tested for the stress at 500% elongation, tensile strength and ultimate elongation. The test pieces exposed to the light through the filter (1) showed serious deterioration even at 40°, but those exposed to the light through the filter (2) showed slow deterioration at 40°, and somewhat marked at 65°. The stress at 500% elongation was somewhat higher in the test pieces exposed to the light through filter (1) than those exposed to the light through the filter (2), showing greater stiffening in the former case. It is concluded that if light is used in the aging test, the selection of the light source is an important question. SHUMPEI OKA

The lamellar packing of rubber. M. KRÖGER. Univ. Leipzig. *Kolloid-Z.* **45,** 47–52(1928).—The paper is the beginning of a study of the capacity for potential energy as a function of the magnitude of deformation, state of cure and temp., a microscopic study of surfaces, the influence of compounding ingredients on longitudinal and lamellar deformation, the optical effects accompanying lamellar deformation in distinction to longitudinal deformation, heat effects, changes of d. during deformation and elec. cond. during lamellar deformation. The absorption of energy in the transformation of rubber to a state of lamellar packing takes place in a different way from the absorption of energy during transformation to rod packing. With increasing deformation, the internal tension passes through a max. and then a min. The capacity for potential energy is at its max. value smaller than in longitudinal stretching. Lamellar effects caused by the addn. of ingredients, which are common to all ingredients of similar particle size, are described. A new app. for observing microscopically the surface configurations during lamellar packing is described. C. C. DAVIS

The double refraction of rubber in the undeformed and in the deformed state. M. KRÖGER. Univ. Leipzig. *Kolloid-Z.* **45,** 52–6(1928).—In its normal undeformed state, raw rubber shows double refraction, but when stretched it shows biaxial positive double refraction. This change is unmistakable as soon as it can be observed in the direction of extension. Vulcanized rubber can be considered to show only uniaxial and biaxial positive double refraction. Lamellar deformation (cf. preceding abstr.) leads in all cases to weak biaxial negative double refraction. C. C. DAVIS

Report on "Revertex." IMPERIAL INSTITUTE. *Trop. Agr.* (Ceylon) **70,** 5–11 (1928).—Revertex is difficult to handle quantitatively. ZnO made into a paste with H_2O can be mixed into revertex merely by stirring. Three revertex mixings: (1) 10% S, (2) 5% S and 5% ZnO and (3) 3% S and 47.5% ZnO, were tested. When the revertex-S mixing was plasticized for the standard time of the Imperial Institute, it was more plastic than plantation rubber, judged by the rate of extrusion (14:18). The mixing high in ZnO took 24 min. to plasticize, while plantation rubber required 30 min. for the same degree of plasticity, 665 watt-hrs. being required to plasticize the revertex and 1025 watt-hrs. to masticate and mix the plantation rubber. No satisfactory est. of the mixing and drying costs of revertex can be given. Revertex mixings easily scorched after addn. of S. After heating at 100° for 20 and 90 min., D_{30} detd. with the plate plastometer was 109 and 168. The revertex-S mixing vulcanized 10 times as quickly as sheet or crepe mixings. In the presence of ZnO, revertex vulcanized nearly as quickly as the corresponding sheet or crepe mixings contg. 1% diphenylguanidine. Continued vulcanizing for 45 min. did not alter the properties of the revertex-ZnO mixing appreciably. The tensile strength, elongation under a load of 1.04 kg. per sq. mm. and slope for the 3 mixings were 2300, 2440 and 2690 lb. per sq. in.; 805, 694 and 573% and 39, 33 and 41, resp. When a revertex-S mixing was vulcanized 8 min. at 148° and then artificially aged in an oven at 70°, the tensile strength increased from 1590 lb. per sq. in. at the start to 2260 after 96 hrs. and then decreased to 1460 after 300 hrs. and to 850 after 600 hrs. The elongation under the load mentioned above remained approx. const. to the end. Crepe and smoked sheet in the same tests decreased in strength from the beginning and much more rapidly than the revertex, and also decreased in elongation after only 144 hrs. Revertex mixings were not superior in tensile strength to the corresponding dry rubber mixings contg. a suitable org. accelerator. A. L. MEHRING

The reclaiming of rubber. A. M. MUNRO. *Chem. Eng. Mining Rev.* **20,** 281 (1928).—A review. E. H.

Seasonal variations in the composition of the latex of Hevea brasiliensis. NORMAN RAE. *Analyst* **53,** 330–4(1928).—Monthly analyses show that the N, K and P_2O_5

contents reach a max. in Feb., decrease slowly till May, increase to July and then decrease to August. Since the leaf fall coincides with the decrease in March and the maturing of the seeds with the drop in July, it seems possible that latex is a food reserve to be used when the leaf and seed growths are most active. W. T. H.

Comments on a thesis (structure of rubber). J. Dugué. *Rev. gén. caoutchouc* **1928,** No. 41, 7–11; cf. *C. A.* **22,** 2682.—Only when the properties of rubber are explained in terms of subatomic phenomena, the application of which is illustrated, will it be possible to obtain knowledge of rubber which can be applied systematically to the solution of technical problems. C. C. Davis

Plasticity determinations in crude rubber. V. Influence of different factors on the changes in plasticity when keeping the rubber. Otto de Vries. Rubberproefstation Nederlandsch-Indië. *Arch. Rubbercultuur* **12,** 243–56(1928). (In English 257–67); cf. *C. A.* **20,** 124.—A study of the varying compn. of latex and the different methods used in prepg. rubber failed to show that variations in the plasticity of the com. product can be explained by these factors (cf. *C. A.* **22,** 2077). The plasticity of raw rubber therefore changes when the latter is kept, so a study was made of the influence of individual factors on these progressive changes in plasticity. The latter plasticity values were detd. when the rubber was new and after 1–2 yrs. When rubber contains below the normal proportion of serum substances, its plasticity increases more on keeping than does that of rubber with a normal quantity of serum substances. The greater the diln. of the latex when coagulated, the greater is the increase in plasticity of the resulting rubber on keeping. This may be a result of the extn. of serum substances by the water. Since rubber which contains all the serum substances becomes harder when kept, and that which contains a deficiency of serum substances becomes softer, there must be an intermediate proportion of serum substances where the plasticity remains practically unchanged while the rubber is kept. This proportion of serum substances is within the range of that normally present in com. plantation rubber (cf. *C. A.* **22,** 2077). The changes in plasticity on keeping are little influenced by the age of the trees from which the rubber was obtained, not even rubber from very young trees changing in any noteworthy manner. Neither does the nature nor the proportion of acid used for coagulation influence these changes in plasticity. Likewise mech. treatment (rolling, milling, sheeting, etc., under different conditions), heating during the drying operation and smoking fail to influence the plasticity in any definite way. On the other hand when a large dose of AcONa is added to the latex, the rubber becomes very weak on keeping, and finely cut, unwashed maturated coagulum also becomes very weak in contrast to crepe from maturated coagulum which becomes harder to about the same extent as does ordinary crepe. No definite influence on the plasticity on keeping could be attributed to coagulation by heating, whereas coagulation by EtOH tends to cause the rubber to become gradually softer. The plasticity of crepe from ammoniated latex changes in about the same way as that of crepe prepd. under the same conditions from fresh latex. Likewise films from ammoniated latex evapd. in the air become very hard on keeping, in the same way as films from fresh evapd. latex. C. C. Davis

Cooling rubber mills. Fred. Grove-Palmer. *Rubber Age* (London) **9,** 141 (1928). C. C. Davis

Rubber vulcanization accelerators in ultra-violet light from the Hanau analytical quartz lamp. Rudolf Ditmar and Wilhelm Dietsch. *Chem.-Ztg.* **52,** 388–9(1928); cf. *C. A.* **22,** 2291; Kirchhof, *C. A.* **22,** 2291.—Exposure of various accelerators to filtered ultra-violet light showed that most of them are readily distinguishable by their characteristic *fluorescence.* When they are mixed in pale crepe without any other ingredient, the fluorescent colors of the mixts. are characteristic enough in some cases to distinguish the accelerators. Even when other ingredients, such as S, ZnO, MgO, PbO, etc., are present, it is possible in some cases to distinguish a characteristic fluorescence, though with several ingredients present, the fluorescent effect varies with the different combinations, and only by knowing the compn. of the mixt. does the particular fluorescence have any significance. C. C. Davis

Reclaimed rubber compounding. A review of progress made along lines of correct vulcanizing, aging and reinforcement in reclaimed rubber compounds. D. F. Cranor. *India Rubber & Tire Rev.* **27,** No. 11, 30, 33–4(1927); cf. *C. A.* **22,** 185.—A crit. review of recent scientific and technical research. Emphasis is laid on the fact that reclaimed rubber may be of inferior quality *per se,* and yet may give disproportionately good results when used as a component in rubber mixts. (cf. Winkelmann, *C. A.* **21,** 511). The discussion deals particularly with papers by Vogt (*C. A.* **22,** 1058) and Bierer and Davis (*C. A.* **20,** 2092). C. C. Davis

Effect of various carbons in rubber. Ellwood B. Spear and Robert L. Moore. *Rubber Age* (London) **9,** 123–5(1928); cf. *C. A.* **20,** 2095.—C blacks may for convenience

be grouped in 4 classes, according to the properties imparted to rubber, the effects being relative only: (1) those which impart great stiffness, high tensile strength and moderate ultimate elongation (channel or gas blacks); (2) those which impart great stiffness, moderate tensile strength and low ultimate elongation (lamp blacks); (3) those which impart little stiffness, moderate tensile strength and moderate ultimate elongation (*e. g.*, thermatomic C), and (4) those which impart little stiffness, high tensile strength and very high ultimate elongation (these blacks are in an exptl. stage, cf. *C. A.* **20,** 2095). Data are presented to illustrate the properties of cured mixts. contg. the different types of C blacks. The radical differences between blacks of classes (1) and (2) on the one hand and of (3) and (4) on the other are especially emphasized. Some C blacks retard the rate of vulcanization, whereas others (class (4)) have a pronounced accelerating action. These effects vary in turn with the type of rubber and with the particular accelerator. C blacks of class (4) are unique in that with certain accelerators, notably diphenylguanidine, and in certain proportions, *e. g.*, 14 parts of C black per 100 parts of rubber by vol., they give mixts. with an ultimate elongation as great as, or even greater than, the basal mixts. contg. no C black. This lends support to the plastic film theory of Wilson applied by Spear to rubber-C black mixts. (cf. *C. A.* **18,** 1064). The ability to add high proportions of C blacks of classes (3) and (4) to rubber renders them particularly serviceable in formulating rubber mixts. resistant to heating. C. C. DAVIS

Patent review. CARL BÖHM V. BORNEGG. *Kautschuk* **1928,** 134–6; cf. *C. A.* **22,** 2489.—Numerous recent patents of various countries on the use of latex, raw rubber, mixing, vulcanization and manufactured products are itemized. C. C. DAVIS

The influence of some gas blacks on the properties of rubber mixtures. [FIRMA] ANTON ANDRÉ SOHN. *Kautschuk* **1928,** 139.—Measurements of the *particle size of C blacks* gave the following values: Brand M and St. (A.A.S.), 60% of 15–40μ, 38% of 40–90μ; Brand No. 200 (A.A.S.), 30% of 15–40μ, 68% of 40–70μ; American, 65% of 15–40μ, 35% of 40–70μ; Thermax, 20% of 15–40μ, 73% of 400–100μ. It is claimed that the A.A.S. blacks impart just as good properties to rubber mixts. as American blacks. C. C. DAVIS

Yellow ocher in the presence of hydrogen sulfide. GORDON EASTWOOD AND A. M. MUNRO. *Chem. Eng. Mining Rev.* **20,** 322–3(1928).—In some expts. on compounding yellow ocher into rubber, one of the rubber compds. came out gray in color instead of yellow. This was apparently due to the formation of a film of Fe_2S_3. On standing in the air this tends to revert back to Fe_2O_3. W. T. H.

Patents

Treating latex. A. BIDDLE. Brit. 277,194, Nov. 10, 1926. See Can. 267,166 (*C. A.* **21,** 1031).

Concentrating rubber latex and similar latices. A. PETERSON. U. S. 1,670,900, May 22. A thin layer of latex is spread on a moving surface such as that of the inner surface of a rotating drum and moisture is removed from the layer without coagulation, the latex thus treated is returned to the bulk supply and this operation is continued until the bulk of material under treatment has reached the desired concn. An app. is described.

Containers (lined with unvulcanized rubber) for shipping rubber latex. E. HOPKINSON. Brit. 277,074, June 7, 1926.

Rubber articles from latex. S. D. SUTTON. U. S. 1,670,598, May 22. In forming gloves, bulbs or other articles, liquid latex is applied to and dried upon a former or mold, thickened or concd. latex is then applied to the surface of the dried latex, and the material is heated so that the outer skin or surface only of the thick or concd. latex is dried; the article is then subjected to the action of C_6H_6 or other suitable rubber solvent or softening agent to produce a superficial effect or design.

Rubber composition. F. C. DYCHE-TEAGUE. U. S. 1,670,599, May 22. A reinforcing agent and filler for rubber consists of C produced by reaction of CO in the presence of Ni and Fe powder or other metal catalyst, together with the catalyst on which it is deposited. Cf. *C. A.* **22,** 1498.

Aging rubber. H. W. ELLEY (TO E. I. DUPONT DE NEMOURS & CO.). Brit. 276,968, Aug. 31, 1926. Aging of rubber is improved by treating it with secondary aromatic amines such as phenyl-α-naphthylamine, ditolylamine, dixylylamine and tolyl-α-naphthylamine in soln. or vapor form, either before or after vulcanizing.

Coating metal surfaces with rubber. DUNLOP RUBBER CO., LTD., A. LAKEMAN AND F. C. MACABE. Brit. 276,705, April 29, 1926. Gutters, structural iron work, automobile bodies or other surfaces are covered with a vulcanized compn. about 75%

of which may be formed of tire scrap and which, in various mixts. and proportions, may also include uncured rubber scrap, S, mineral oil, "brown substitute," PbO, lime, whiting, stearic acid and $MgCO_3$.

Coloring rubber. I. G. FARBENIND. A.-G. Brit. 277,034, Sept. 4, 1926. Insol. metal salts of triarylmethane dyes having a sulfo group in *o*-position to the methane C atom, or of a sulfonic acid or carboxylic acid of an anthraquinone deriv. having at least one free or substituted amino group, are mixed with rubber before vulcanizing. Several examples are given.

"Non-skid" patterns on crepe rubber surfaces. ST. HELENS CABLE & RUBBER CO., LTD. AND H. C. HARRISON. Brit. 276,763, June 17, 1926. A frame of woven wire or the like may be heated and pressed into the rubber or the rubber itself may be heated and the frame pressed in cold. Various details are given.

Planographic printing surfaces formed of rubber. W. C. HUEBNER. U. S. 1,669,416, May 15.

Condensation system for recovery of volatile solvents from rubber, etc. A. BOECLER. Brit. 276,694, Aug. 30, 1926.

Regenerating waste rubber. SYNDICAT FRANCO-NEERLANDAIS. Brit. 276,626, Aug. 25, 1926. Material of tire casings or the like is impregnated with oil obtained by distg. waste rubber, further treated with HCl to polymerize the oil and swell the material, washed with water, slitted and sepd. from the hard core and then further treated to effect regeneration.

Apparatus for making vulcanized fiber sheets. G. W. TEMPLE. U. S. 1,669,429, May 15.

Rubber vulcanization accelerators. C. M. CARSON (TO GOODYEAR TIRE & RUBBER CO.). Brit. 277,338, Sept. 7, 1926. Mercaptobenzothiazyl disulfide or other sulfides of the thiophenols, aminothiophenols, thiazoles, etc., are prepd. by treating the mercaptan or its salts with S chloride. The products may be used as accelerators alone or with amino compds.

Vulcanizing rubber tubes and other articles. L. A. LAURSEN. Brit. 276,430–1, May 27, 1926. Mech. features.

Vulcanizing rubber. C. O. NORTH and C. W. CHRISTENSEN. U. S. 1,670,312, May 22. The reaction product of aniline and crotonaldehyde is used as an accelerator.

Vulcanizing rubber. E. I. DUPONT DE NEMOURS & CO. Brit. 276,435, May 28, 1926. Accelerators are prepd. from an aldehyde, an amine and CS_2 or from an anhydroaldehyde amine and CS_2 or from an aldehyde and the substituted NH_4 salt of a monosubstituted dithiocarbonic acid. The mol. proportions of aldehyde, amine and CS_2 may be 1:1:1, 2:1:1, 2:2:1 or 4:2:1. Aldehydes such as CH_2O, AcH, propionaldehyde, butyraldehyde or benzaldehyde may be used and among the suitable amines are: methylamine, ethylamine, hydroxyethylamine, *n*- or iso-propylamine, *n*- or iso-butylamine, aniline or *o*- or *p*-toluidine. Several detailed examples are given.

Vulcanized pitch. W. SAVAGE. U. S. 1,669,490, May 15. A soft rubber-like compn. adapted for use on roads, tanks or roofs, etc., is formed from fatty acid "still bottoms" residue vulcanized with S and an accelerator such as $PhNH_2$, thiocarbanilide, ZnO or MgO. U. S. 1,669,491 specifies a vulcanizing agent contg. an active alk. substance such as basic Mg carbonate.

Rubber. G. H. CARNAHAN (to Intercontinental Rubber Products Corporation). U. S. 1,671,570, May 29. Guayule plant or similar material is ground in successive stages with different proportions of water, to sep. rubber, bagassee and "cork." An app. is described.

Coagulating latex. BATAAFSCHE PETROLEUM MAATSCHAPPIJ AND F. R. MOSER. Brit. 278,395, April 7, 1926. Natural emulsions such as rubber latex are coagulated by the method described in Brit. 245,418 (*C. A.* **21**, 319). Rubber latex contg. NH_3 is added to a soln. of $AlCl_3$ and the colloidal $Al(OH)_3$ formed produces a protected dispersion of the latex. Fillers, vulcanizers, accelerators, preservatives and the like may be added.

Treating latex, etc. K. D. P., LTD. Brit. 277,373, Sept. 10, 1926. Latex or similar material (which may be mixed with fillers) is dried while continuously exposing new surfaces and heating the mass, *e. g.*, on rollers or endless belts or by slitting and folding a rolled sheet.

Compounding latex with fillers. K. D. P., LTD. Brit. 277,374, Sept. 10, 1926. In compounding latex with active fillers such as lampblack the filler is added while the latex is manipulated continuously to expose fresh surfaces and with simultaneous drying. A mixt. may be formed of rubber as latex 100, tar 5, ZnO 20, S 3, and palm oil 0.6 parts and 200 parts of gas black may be added to this gradually while drying.

Rubber coatings. K. D. P., LTD. Brit. 277,375, Sept. 10, 1926. Surfaces such as those of wood, metal, stone or leather are sprayed with latex and water is simul-

taneously evapd. from the latex by application of heat. The compn. of the latex may be varied during the spraying to produce films of varying characteristics.

Molded rubber articles from latex. E. A. HAUSER (to K. D. P., LTD.). Brit. 277,376, Sept. 10, 1926. Latex is sprayed onto the surface of a mold and water is simultaneously evapd. by heating. Artificial dispersions as well as natural latex may be used and auxiliary ingredients may be added and reinforcing fabrics or the like may be embedded in the material for making tires or other articles.

Composite rubber sheet patches for tires, etc. R. D. KAMDIN and J. LEADBITTER-SMITH. Brit. 278,192, Oct. 25, 1926. A glass plate or former is dipped into rubber soln. to form a layer and a sheet of vulcanized rubber previously treated with rubber soln. until tacky is pressed on the layer. Subsequently the materials are stripped from the glass.

Fiber-reinforced rubber articles. W. B. WESCOTT (to Rubber Latex Research Corporation). U. S. 1,671,914, May 29. Fibrous material such as a "fabric," felt or bat is passed through a latex bath into an acid bath, coagulation is permitted, the article is pressed to remove water, washed, and dried *in vacuo* to a subnormal moisture content at about 65° and compressed while still warm.

Polymerized vinyl alcohol. W. O. HERRMANN and W. HAEHNEL (to Consortium für elektrochemische Industrie). U. S. 1,672,156, June 5. Vinyl esters such as the acetate or propionate are polymerized, *e. g.*, by use of benzoyl peroxide, and the polymerized esters are treated with an alk. reagent such as KOH and alc. Cf. *C. A.* **21**, 3369; Whitby, McNally and Gallay, *C. A.* **22**, 2079.

Rubber-like polymerized terpene product. W. B. PRATT (to Dispersions Process, Inc.). U. S. 1,671,314, May 29. A polymerized terpene of the general type formula $(C_5H_8)_n$ capable of reacting with S and which may be formed from isoprene is dispersed in particles of colloidal size coated with hydrophilic protein films such as albumin or casein and the latter are tanned, *e. g.*, by use of tannin, to increase their strength and toughness, the particles are coagulated and the coagulated mass is sepd. and dried. The product thus obtained is suitable for some uses similar to those of rubber.

Vulcanizing balls, tire tubes or other closed hollow rubber articles. W. L. FAIRCHILD. Brit. 277,410, June 14, 1926. Mech. features.

Apparatus for vulcanizing rubber tires. AKRON STANDARD MOLD CO. Brit. 277,851, Jan. 6, 1927.

Apparatus for vulcanizing tire tubes, etc. O. J. KUHLKE (to Kuhlke Co.). Brit. 277,934, Sept. 21, 1926.

Vulcanizing rubber. W. P. TER HORST (to Rubber Service Laboratories Co.). U. S. 1,672,548, June 5. A tetrasubstituted guanidine such as dipiperidylguanidine is used as an accelerator.

Vulcanizing rubber. L. B. SEBRELL (to Goodyear Tire & Rubber Co.). Brit. 278,689, Oct. 8, 1926. Vulcanization accelerators comprise reaction products of mercaptans or their derivs. and basic N compds. such as NH_3 or di-Et, Pr and Bu amines, *e. g.*, the reaction product of mercaptobenzothiazole and ethylenediamine or the diphenylguanidine salt of mercaptobenzothiazole. Cf. *C. A.* **22**, 512.

Vulcanizing rubber. L. B. SEBRELL and C. W. BEDFORD. Can. 277,225, January 17, 1928. Rubber is vulcanized in the presence of a metallic salt of mercaptothiazole.

Vulcanizing rubber. P. M. PAULSON. Can. 276,866, January 3, 1928. Rubber is combined with a vulcanizing agent and an accelerator consisting of a guanidine substituted on but 1 N atom and whose substituents contain a total of more than 6 C atoms.

Vulcanizing rubber. LIVERPOOL RUBBER CO., LTD. AND F. AMENDE. Brit. 278,064, June 26, 1926. An app. is described comprising a vulcanizing chamber heated by steam pipes or the like and also by preheated air or other gas which is circulated through the chamber.

Preventing adhesion of unvulcanized rubber sheets. K. MEDGYES. Brit. 277,928, Sept. 25, 1926. Dusting prepns. are used which lose their anticohesive properties when the sheets are die-stamp welded with hot tools, so that there is no weakening of the welded seams. Among the substances which may be used are: $C_{10}H_8$, acetanilide (in alc. soln.), $(CH_2)_6N_4$, thiocarbanilide (in aq. suspension) and org. metal salts such as fatty acid salts of Pb or Zn.

Rubber-like vulcanized polymeric vinyl compounds. W. O. HERRMANN and W. HAEHNEL (to Consortium für elektrochemische Industrie). U. S. 1,672,157, June 5. Polymerized products such as may be obtained from vinyl alc. or vinyl acetate are vulcanized with S chloride. Cf. *C. A.* **21**, 3767; Whitby, McNally and Gallay, *C. A.* **22**, 2079.

Reclaiming and dispersing vulcanized rubber. T. G. RICHARDS and G. P. F. SMITH (to Dispersions Process, Inc.). U. S. 1,671,316, May 29. The material is heated under pressure with an alkali such as NaOH soln. and with "cumar" or other

softener and resin oil to produce a plastic mass contg. sufficient soap, formed *in situ*, to permit dispersion by manipulation in water, and dispersion in water is then effected, to obtain a product which is suitable for use as a reclaimed rubber.

Treating latex. M. R. Day (to Rubber Latex Research Corporation). Brit. 279,336, Jan. 3, 1927. Stabilization of latex is effected by adding a small proportion of blood or its constituents such as defibrinated blood, serum or "red end" (hemoglobin). The product may be coagulated by acids when desired but does not coagulate by agitation or addn. of fillers.

Treating latex. W. A. Gibbons and J. McGavack (to U. S. Rubber Plantations). U. S. 1,673,672, June 12. Latex is treated with a material such as a salt of sulfonated undecylinic acid which prevents coagulation but permits bacterial action and is allowed to stand until the protein constituents of the latex are substantially decompd. and is then dried to form a film which has a pitted surface and is substantially transparent.

Rubber latex packing or gaskets. F. Carl. Brit. 279,342, May 24, 1927. In making packings, gaskets, bottle closures and the like as described in Brit. 259,987 (*C. A.* **21,** 3490), the fillers are omitted and thickened or concd. vulcanized latex is used with or without addn. of unvulcanized latex. S, ZnO, etc., may be used for vulcanizing.

Uniting fabric seams with latex. C. C. Loomis and G. E. Perry (to U. S. Rubber Co.). U. S. 1,673,573, June 12. A partially coagulated latex in paste form and contg. vulcanizing ingredients is applied between superposed fabric edges such as those of cotton or jute and the material is pressed and vulcanized.

Electrodeposition of rubber, etc. Anode Rubber Co., Ltd. Brit. 279,474, April 15, 1926. In electrodeposition of rubber or the like from dispersions, substances are incorporated with porous molds which increase the cohesion of the rubber particles, *e. g.*, compds. of Ca, Mg, Ba, Zn, Fe or Al, or highly absorptive org. bases, esters or urethans. The addn. of NH_3 or NH_4 salts assists soln. and renders the soln. alk. Carbonates produced in molds are removed by an acid to prep. the molds for further use.

Retarding oxidation of rubber. S. M. Cadwell (to Naugatuck Chemical Co.). U. S. 1,673,549, June 12. Before vulcanization there is incorporated with rubber an accelerating aldehyde-aliphatic amine condensation product in excess of that required to secure proper vulcanization. Cf. *C. A.* **21,** 2200.

Sponge rubber. T. W. Miller (to Fautless Rubber Co.). U. S. 1,674,053, June 19. A quantity of vulcanized sponge rubber particles is incorporated into unvulcanized sponge rubber stock together with addnl. "blowing agent" and the mixt. is formed and vulcanized.

Rubber articles from aqueous rubber dispersions. M. C. Teague (to American Rubber Co.). U. S. 1,673,649, June 12. In forming coatings or other articles a body of dispersion such as latex is disposed in a relatively thick layer in the presence of a hydrophilic agent such as glycerol or an NH_4 soap and is exposed to drying conditions so that moisture is substantially uniformly withdrawn from all parts of the body without formation of a dried surface film.

Tanks lined with guayule or its mixtures with rubber, etc. Soc. electromecanique d'appareillage pour l'essence. Brit. 279,291, Dec. 31, 1926.

Vulcanization. D. H. Powers. Can. 278,942, Mar. 27, 1928. Rubber is combined with a vulcanizing agent and a compd. obtainable by the chem. combination of not less than 2 mols. of an aldehyde and 2 mols. of a primary amine with a whole number of mols. less than 3 of CS_2.

Vulcanizing rubber. D. H. Powers (to E. I. du Pont de Nemours & Co.). U. S. 1,674,122, June 19. Oxyethyl- (or butyl-) thiocarbonic monosulfide or similar compd. is used as an accelerator. Conjoint use of an amine such as aniline further expedites the vulcanization.

Vulcanizing rubber. A. C. Burrage. Brit. 279,280, Jan. 4, 1927. As an accelerator there is used an aryl substituted guanidine having an alkyl substituent in the *o*-position, *e. g.*, di-*o*-tolylguanidine (which may be made by heating di-*o*-tolylthiourea, produced by the reaction of CS_2 on *o*-toluidine, with PbO in the presence of NH_4NO_3 and alc. and neutralizing the filtrate with NaOH). Cf. *C. A.* **21,** 1724.

Vulcanizing rubber. S. M. Cadwell (to Naugatuck Chemical Co.). U. S. 1,673,550, June 12. Dimethylthiocarbamyl-*p*-toluenethiolsulfonate or other compds. contg. the group $S.SO_2$ are used as accelerators.

Accelerator for vulcanizing rubber. H. O. Chute. U. S. 1,673,801, June 19. In prepg. an accelerator, magnesia and an aromatic amine such as aniline are mixed without heating and CS_2 is gradually added while keeping the mixt. cold and without evolution of substantial quantities of H_2S and the material is then heated to a temp. not exceeding 140° until evolution of gas has substantially ceased.

Vulcanization accelerator. W. Scott. Can. 278,941, Mar. 27, 1928. A rubber-vulcanization accelerator is made by treating with CH_2O the condensation product of aniline and a straight-chain aldehyde contg. a plurality of C atoms.

Apparatus and method for vulcanizing rubber tire tubes, etc. W. L. Fairchild. U. S. 1,673,352–3, June 12. Steam is injected into the tube for vulcanization and the tube is subjected to a swinging movement to dislodge any deposits of water which may condense within the tube.

Rubber compound. A. M. Kinney. Can. 280,213, May 15, 1928. A rubber compd. contains rubber, vulcanizing constituents and naphthenic compds.

Adhesive rubber composition. M. C. Teague. Can. 280,523, May 29, 1928. An adhesive compn. comprises an aq. suspension of rubber and an emulsified resinous polymerization product of a higher fraction of coal tar distillate.

Rubber-like synthetic product. J. Baer. Brit. 279,406, Oct. 20, 1926. An elastic rubber-like product is obtained by the polymerizing action of S or S-yielding compds. such as alkali sulfides upon satd. halogenized hydrocarbons of the C_nH_{2n+2} group, *e. g.*, methylene or ethylene dichloride, dibromide or iodide. Several examples are given.

Gum composition. Meiji Gum Co., Ltd. Jap. 69,058, Aug. 7, 1926. Plant fiber and wood are dried and powdered. Gum, distd. matter or latex is absorbed by the powder, wax, asphalt, etc., are added, the mixt. is heated and pressed, then rubber and vulcanizer are added and the mixt. is vulcanized by heating. Soft or hard gum compn. is obtained.

Treating rubber stock. Henry R. Minor (to General Carbonic Co.). U. S. 1,675,124, June 26. Solidified CO_2 is used to control the temp. of rubber during processing.

Apparatus for drying rubber, etc., in circulating air. Tomlinsons (Rochdale), Ltd. and E. W. Smith. Brit. 280,016, Oct. 14, 1926.

Apparatus for calendering rubberized sheet material. Arthur A. Frank (to The Fisk Rubber Co.). U. S. 1,674,772, June 26.

Finishing rubber articles. Seaphes D. Shinkle (to The Dominion Rubber Co., Ltd.). Can. 281,123, June 19, 1928. Vulcanizable articles are finished by coating with a varnish, comprising boiled linseed oil and S, vulcanizing and first subjecting the article to a circulating gaseous current contg. S_2Cl_2 and then to a gaseous current contg. NH_3.

Rubber shoe soles. L. C. Bateman. Brit. 279,531, June 26, 1926. Crepe or sheet rubber is used together with sheet material obtained by impregnating woven, felted or loose fibers with latex, drying and consolidating under heat and pressure.

Rubber vulcanization accelerators. S. M. Cadwell (to Naugatuck Chemical Co.). Brit. 279,815, Nov. 1, 1926. Vulcanization is accelerated by use of halogen derivs. of aldehyde-amine condensation products such as those obtained from aliphatic aldehydes contg. 2–7 C atoms by condensation with a primary amine. Numerous examples are given.

Coagulating latex. R. Koepp & Co. Brit. 280,639, Aug. 18, 1926. A soln. of Na biformate is used as a coagulant, with or without other coagulants.

Compositions comprising rubber and fibrous material. William G. O'Brien (to Goodyear Tire & Rubber Co.). U. S. 1,676,798, July 10. Rubber is pptd. on fibrous material and liquid from a suspension of the coated fibers is passed through a screen of sufficiently small mesh to retain the fibers and the latter are then treated with a rubber precipitating agent such as alc. which is passed through the screen.

Belt or rubber and rubberized fabric reinforced with twisted cords. Austin A. Trisher (to Goodyear Tire & Rubber Co.). U. S. 1,676,845. July 10.

Sheet material containing rubber and fiber. Reed P. Rose (to General Rubber Co.). U. S. 1,675,959, July 3. A material suitable for various purposes is formed by mixing a suspension of beaten fibers and an aq. dispersion comprising rubber and protective agent having a negative charge, in an alk. medium, such as a Na resinate soln. and then acidifying the mixt. to reverse the charge on the protective agent and effect deposition of the rubber on the fiber, and forming the material into sheets.

Rubber sheet material with fibrous backing. Tod J. Mell (to B. F. Goodrich Co.). U. S. 1,677,284, July 17. Material suitable for use as a floor covering is formed of a rubber sheet with a backing comprising wool felt or other suitable fibrous material consolidated with bituminous material or other binder which will absorb a rubber solvent such as gasoline without swelling.

Sheet rubber reinforced with wire netting. Bernard A. Ruhling. U. S. 1,677,-372, July 17. Sheets are described which are suitable for use in making automobile bodies, etc.

Apparatus and method for making rubber tubes. John A. Fleischli (to Cupples Co.). U. S. 1,676,776, July 10.

Coating metal with rubber. ALLAN B. MERRILL (to B. F. Goodrich Co.). U. S. 1,677,360, July 17. In making composite sheets, the metal is coated with a tough heat-plastic isomer of rubber such as that formed by heating rubber with phenolsulfonic acid, and a S-contg. rubber compn. is superposed on the coated metal with an intervening layer of material such as a rubber compn. or balata or gutta percha which will inhibit migration of S to the metal; the assembled material is subjected to vulcanization.

Rubber composition for golf-ball centers. PAUL S. SHOAFF (to Goodyear Tire & Rubber Co.). U. S. 1,676,841, July 10. A mixt. of balata resin and scrap vulcanized rubber is heated to reduce it to a gel-like consistency, PbO or other weighting material and S are added, and the product is vulcanized.

Apparatus for vulcanizing rubber articles. CLIFFORD H. OAKLEY. U. S. 1,677,200, July 17.

Apparatus for continuous vulcanizing of rubber heels, etc., under pressure. CLIFFORD H. OAKLEY. U. S. 1,677,201, July 17.

Vulcanizing rubber. ALBERT C. BURRAGE, JR. U. S. 1,677,169, July 17. Diphenyl-*o*-tolylguanidine or other tri-substituted guanidine contg. phenyl and tolyl substitution radicals is used as an accelerater. Cf. *C. A.* **22**, 2856.

Vulcanizing rubber. RALPH V. HEUSER. U. S. 1,677,235, July 17. *o*-Tolyl-di-*p*-tolylguanidine or other suitable substituted guanidine contg. an aryl group in each of the amino positions and a *p*-substituted aryl group in the imino position is used as an accelerator.

Vulcanizing rubber. BRITISH DYESTUFFS CORPORATION, LTD., C. J. T. CRONSHAW and W. J. S. NAUNTON. Brit. 280,661, Sept. 3, 1926. Rubber is given good aging properties by use of a condensation product of equal proportions of α- and β-naphthylamine with AcH formed in the presence of an acid such as HCl. About 1.5% of this condensation product may be added to rubber compns. before vulcanizing.

Vulcanizing rubber. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,676,838, July 10. The product of crotonaldehyde, acetaldehyde and aniline or other suitable reaction product of an unsatd. aldehyde, a satd. aldehyde and an amine is used as an accelerator.

Rubber. SOC. DU CAOUTCHOUC ANODEX. Fr. 632,144, April 5, 1927. To prevent liberation of gas at the cathode in the electrophoretic deposition of rubber, the surface of the cathode is formed of an easily reducible metallic oxide such as PbO_2 and the cathode itself is preferably of Pb. An app. is described.

Rubber. THE B. F. GOODRICH CO. Fr. 632,474, Oct. 30, 1926. Addn. to 599,561. Fragments of rubber are treated with a sulfonyl chloride such as *p*-toluenesulfonyl chloride to produce a product plastic when heated.

Treating rubber latex. OMAR H. SMITH (to General Rubber Co.). U. S. 1,678,022, July 24. Latex is thickened with a buffer soln. such as a mixt. of primary and secondary Na phosphates, water-sol. substances are sepd. by stratification and a purified dispersible product is obtained.

Deposition of rubber. SOC. DU CAOUTCHOUC ANODEX. Fr. 632,143, April 5, 1927. The deposition molds used in the electrophoretic deposition of rubber are treated after use to recover their efficiency. If of unglazed clay they are heated to incandescence, or they are placed in an electrolytic bath contg. no colloid and current is passed in the opposite direction to that of the deposition, or they are washed under pressure with an alk. soln. or with the same electrolyte used for the impregnation of the molds in such a way that the liquid passes through the mold from the side which is turned towards the anode in the bath. If Ca salts have been added to the electrolytic bath the molds are washed with HCl. The amount of Ca salts required may be reduced by adding Mg compds.

Preserving rubber. J. TEPPEMA (to Goodyear Tire and Rubber Co.). Brit. 281,616, Nov. 30, 1926. The aging qualities of rubber are improved by the addition of reaction products of phenols and amines such as phenyl α- or β-naphthylamine, α,β-dinaphthylamine, β,β-dinaphthylamine or diaminodiphenyldi-β-naphthylmethane. Directions are given for making these compds. and tables are given showing their effects when used with rubber.

Rubber composition. LORIN B. SEBRELL (to The Goodyear Tire and Rubber Co.). Can. 282,347, Aug. 7, 1928. Rubber is preserved by vulcanizing in the presence of a reaction product of an aldehyde and an amine formed at a temp. of approx. 0° and which is substantially a non-accelerator.

Rubber composition. LORIN B. SEBRELL (to The Goodyear Tire and Rubber Co.). Can. 282,348, Aug. 7, 1928. Vulcanized rubber is preserved by incorporating therein a reaction product of a crotonaldehyde and an aromatic amine, which is substantially a non-accelerator.

Rubber composition for facing molds. ADRIAN BAISH. U. S. 1,677,881, July 24.

Molds suitable for forming rubber balls or other articles are faced with a compn. of rubber, S, Zn dimethyldithiocarbonate, methyl mustard oil, a filler, a "lightener" and a drier, *e. g.*, lime, clay, ZnO, MgO or $MgCO_3$ or asbestos.

Regeneration of waste rubber. WALDEMAR SCHEITHAUER. Fr. 632,990, April 20, 1927. See Brit. 270,675 (*C. A.* **22,** 1706).

Vulcanizing rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,678,084, July 24. The CS_2 deriv. of the reaction product of diethylamine with paraformaldehyde is used as an accelerator in vulcanizing rubber with S. U. S. 1,678,085 specifies the similar use of the CS_2 deriv. of the reaction product of piperidine and furfuraldehyde.

Making and vulcanizing inner tubes of pneumatic tires. ERNEST W. MELVIN (to Fisk Rubber Co.). U. S. 1,678,015, July 24. Mech. features.

Rubber substitute. MORTIMER T. HARVEY. Fr. 632,454, Oct. 20, 1926. Addn. to 622,963. Cashew nut oil and glycerol are mixed and heated to about 245° to obtain a product similar to rubber, which can be vulcanized.

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Plasticity and Elasticity of Rubber

A. van Rossem and H. van der Meijden *

PLASTICITY determinations of raw and masticated rubber have in recent years attracted a great deal of the rubber chemists' attention, as the publications of Marzetti[1], Williams[2], De Vries[3], Griffiths[4] and others have proved. In various laboratories, plasticity measurements have even become routine tests for raw and masticated rubber.

There are, generally speaking, two methods of determining the plasticity of rubber, viz.:

(1) The extrusion method, in which the masticated dough is extruded through an orifice (Marzetti), and the extruded portion weighed. This method can be used only for masticated rubber and rubber mixings.

(2) The compression method, in which a piece of raw or masticated rubber is compressed and the decrease in thickness is measured.

The latter method has been used in the past by many investigators for plasticity measurements of various substances, *e.g.*, by Speedy[5], who as long ago as 1920 carried out plasticity determinations on gutta-percha, balata, and various bitumens with the Widney resiliometer, an apparatus based on the compression principle. Williams[2] was the first to apply this method, in 1924, to the determination of the plasticity of rubber, and since then De Vries[3] especially has made use of this method in his extensive investigations of the plasticity of raw rubber.

In the Netherland Government Rubber Institute also, plasticity

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measurements have been made according to this second method. The plastometer used for these experiments was constructed by J. A. C. van Kampen, instrument maker of the laboratory of Technical Botany, Technical University, Delft. For the details of its construction reference may be made to the publication of De Vries[3], who used the same instrument.

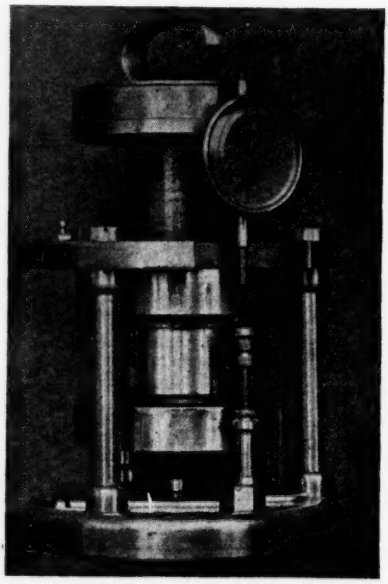

Fig. 1—Plastometer with Loose Plate and Platform

One important alteration was made in the instrument. Most of the previous investigators have compressed the rubber between two parallel plane surfaces and have measured the decrease in thickness in relation to time. During such measurements the surface of the rubber under pressure is continuously increasing, and therefore the pressure per unit of surface is continuously diminishing.

Bingham[6], who more than any other investigator has contributed towards the theory of plasticity, always used a constant pressure per unit surface in his experiments. It seemed advisable, therefore, to have a constant pressure per unit surface in our plasticity experiments. This condition is easily fulfilled by pressing the rubber on a platform of 1 sq. cm surface, screwed into a loose ground plate. In this way the rubber flows from the platform and only a constant area is pressed.

Fig. 1 gives a photograph of the plastometer, the loose plate with platform being clearly visible.

The decrease in thickness of the rubber is measured by a gauge, which reads to 0.01 mm., and the plastometer can be used at any temperature by making use of a constant temperature thermostat or drying oven with glass window.

Various investigators carrying out plasticity measurements have simply determined the curve of decrease of thickness in relation to time of pressure, and have used the thickness of the rubber after an arbitrary period of time as a measure of plasticity[7]. It may be pointed that such curves do not establish the plasticity of the material under investigation.

Maxwell[8] gave the following definition of plastic bodies: "If the form of a body is found to be *permanently* altered when the stress *exceeds a certain value*, the body is said to be soft or plastic." It is particularly the permanency of this alteration of form, which decides whether plasticity or some other physical property is measured.

If the alteration in form is not permanent, the substance is either viscous or elastic. It is therefore of great importance in plasticity measurements not only to measure the decrease in thickness, but also to observe any recovery when the applied weight is raised[9], and to measure the recovery in relation to time.

Bingham[10], in his excellent treatise on *Plasticity and Elasticity*, distinguishes three possibilities in regard to deformation under shearing stress:

(1) *Elasticity.*

Deformation occurs instantaneously and after removing the stress recovery is instantaneous.

(2) *Plastic flow.*

After removing the stress, there is no recovery.

(3) *Pseudo elastic flow.*

After removing the stress, a slow recovery (the so-called elastic after-effect) occurs.

These considerations have been applied to our plasticity determinations on rubber. The following is a brief outline of the results obtained with masticated and with vulcanized rubber.

Masticated Rubber

First latex crepe was masticated for 15 minutes. With a plastometer of the type just described the compression curve, *i.e.*, the decrease in thickness of the rubber under a constant load of 5 kgs. per sq. cm., was determined at increasing temperatures. The results of these determinations are shown in Table 1 and graphically represented in Fig. 2.

It is obvious from the results that masticated rubber becomes softer with increasing temperature.

From the considerations advanced above, it is evident that the curves in Fig. 2 do not establish the plasticity of masticated rubber.

TABLE 1. INFLUENCE OF TEMPERATURE ON THE COMPRESSION OF MASTICATED RUBBER. FIRST LATEX CREPE MASTICATED 15 MIN.

Time	Thickness of rubber in 0.01 mm. at 16°C.	at 30°C.	at 45°C.	at 50°C.	at 60°C.	at 70°C.
After 1 min.	160	132	110	85	66	55
After 2 min.	153	123	94	73	54	43
After 3 min.	147	116	85	65	48	37
After 4 min.	144	110.5	78	58.8	44	33
After 5 min.	141	106.5	73	55.1	41.5	30.5
After 6 min.	138.5	103	68	52	39.4	28
After 7 min.	136	100	65	50.2	37.2	26
After 8 min.	134	97.9	62	48.4	35.6	25
After 9 min.	132.5	96.3	59.5	47.0	34	23.8
After 10 min.	131	94.5	57.8	45.5	33	22.5
After 11 min.	129.5	92.8	56	44.2	32.0	21.8
After 12 min.	128	91.5		43.0	31.0	20.8
After 13 min.	126.7		54	42.0	30.0	20
After 14 min.	125.5	89	52.5	41.2	29.3	19.2
After 15 min.	124.5	87.8	51	40.5	28.7	18.8
After 16 min.	123.5	86.6	50.1	39.9	28.0	18.0
After 17 min.	122.6	85.5	49.2	39.0	27.3	17.5
After 18 min.	121.7	84.4	48.3	38.2	26.8	17.0
After 19 min.	120.8	83.6		37.5	26.2	16.7
After 20 min.	119.9	82.9	47.0	36.8	25.8	16.3
After 21 min.	118.8	81.9				15.9
After 22 min.	118	81.2	45.8			
After 23 min.	117	80.7	45.1			
After 24 min.	116	80.0	44.5			
After 25 min.	115.2	79.3	44			
After 26 min.	114.5	78.5	43.5			
After 27 min.	114.0					

These curves might be given equally well by a highly viscous material such as bitumen, or by a soft elastic material. Therefore the recovery of the compressed rubber was studied at the same temperatures. The results obtained at 16°C., 45°C., and 70°C. have been compiled in Table 2, while the results at 16°, 30°, 45°, 50°, 60° and 70°C. are all graphically represented in Fig. 3.

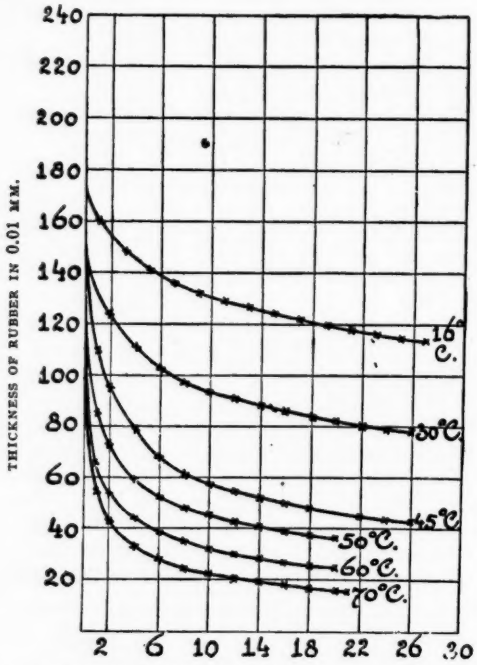

Fig. 2—Time of Pressure in Min. Influence of Temperature on the Compression of Masticated Rubber

TABLE 2. RECOVERY OF COMPRESSED RUBBER SLABS AT VARIOUS TEMPERATURES. THICKNESS IN 0.01 MM.

Temperature 16°C. Original thickness 210 Compressed to 115		Temperature 45°C. Original thickness 218 Compressed to 44		Temperature 70°C. Original thickness 190 Compressed to 17	
After 1 min.	130	After 1 min.	46	After 1 min.	22
After 5 min.	155	After 3 min.	57	After 7 min.	27
After 10 min.	173	After 8 min.	64	After 20 min.	27
After 15 min.	178	After 13 min.	71	After 30 min.	28
After 20 min.	183	After 18 min.	80	After 1 h.30 min.	30
After 25 min.	189	After 23 min.	84	After 2 h. 30 min.	32
After 30 min.	192	After 28 min.	86	After 3 hours	32
After 40 min.	197	After 1 h. 35 min.	11[illegible]	After 4 h. 30 min.	33
After 45 min.	198	After 1 h. 48 min.	117	After 5 h. 30 min.	33
After 50 min.	199	After 2 hours	119	After 24 hours	35
After 1 hour	201	After 2 h. 30 min.	123	After 3 x 24 hours	35
After 1 h. 5 min.	202	After 3 h. 30 min.	125		
After 1 h. 20 min.	205	After 4 hours	126		
After 1 h. 30 min.	207	After 5 hours	127		
After 1 h. 50 min.	209				
After 2 hours	210				
full recovery		part recovery		small recovery	
elasticity		elastic after-effect		plasticity	
elastic after-effect		plasticity			

At 16°C. we see a small elastic recovery, followed by a large elastic after-effect; in 130 minutes the original thickness is fully recovered. At 30° C. the recovery takes 200 min., but at 45°C. there is only partial recovery, and therefore at this temperature masticated rubber is partly plastic. At 60°C. plasticity is still more marked, and at 70°C. there is only a very small elastic after-effect and the material is practically fully plastic.

It is obvious, that the compression curves alone are misleading, since masticated rubber at 16°C. does not show real plasticity, but only pseudo-plastic flow, with an elastic after-effect, while the same rubber at 70°C. shows real plasticity, practically no elastic after-effect being visible after removing the pressure.

Vulcanized Rubber

For various reasons, which may be omitted here, it seemed likely that vulcanized rubber at high temperatures possessed a certain

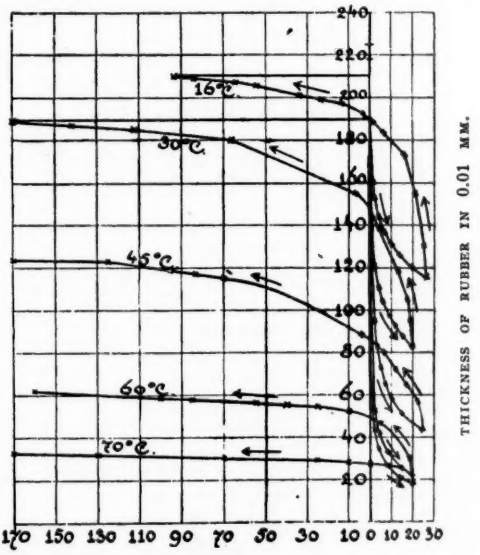

Fig. 3—Elasticity and Plasticity of Masticated Rubber at Various Temperatures

amount of plasticity. To investigate this possibility, plasticity determinations have been carried out with vulcanized rubber of increasing degree of vulcanization.

A mixing of 92.5 parts of first latex crepe and 7.5 parts of sulfur was vulcanized during increasing times of cure ranging from 30 to 240 minutes at 147°C.

With the plastometer the relation of compression to time of pressure was determined at various temperatures, *e.g.,* 18°, 100°, 130°, and 147°C.

The results obtained at a temperature of 147°C. have been represented graphically in Fig. 4. As has been pointed out above, these curves do not establish plasticity, and therefore the recovery has been studied at 18°, 100°, 130°, and 147°C.

TABLE 3. ELASTICITY AND PLASTICITY OF VULCANIZED RUBBER AT VARIOUS TEMPERATURES.

(Mix: First Latex Crepe: 92.5 parts; Sulfur: 7.5 parts)

Time of cure	Total compression 100 Per Cent	Elastic compression Per Cent	Elastic recovery Per Cent	Elastic after-effect Per Cent	Plasticity or permanent set Per Cent
		at 18°C.			
30 min.	100	78	59	37	4
60 min.	100	83	81	19	0
90 min.	100	87	89	11	0
120 min.	100	93	93	7	0
150 min.	100	93	100	0	0
240 min.	100	95	100	0	0
		at 100°C.			
30 min.	100	84	62	18	20
60 min.	100	88	85	15	0
90 min.	100	93	95	5	0
120 min.	100	96	94	6	0
150 min.	100	96	93	7	0
240 min.	100	97	100	0	0
		at 130°C.			
30 min.	100	74	23	53	24
60 min.	100	84	71	14	15
90 min.	—	—	—	—	—
120 min.	100	83	75	23	2
150 min.	—	—	—	—	—
240 min.	100	92	92	8	0
		at 147°C.			
30 min.	100	82	21	25	54
60 min.	100	71	38	24	38
90 min.	100	76	45	32	23
120 min.	100	71	55	18	27
150 min.	100	75	61	16	23
240 min.	100	70	65	7	28

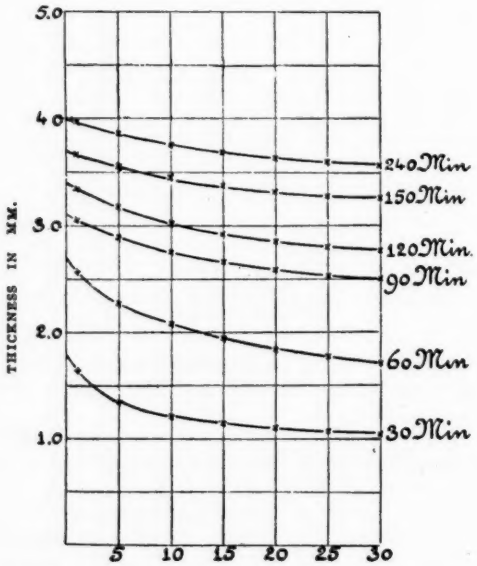

Fig. 4—Relation between Compression and Time of Pressure at 147°C. for Vulcanized Rubber of Increasing Time of Cure

For the sake of brevity the tables containing the measurements

of recovery with time will not be reproduced here. The measurements at 147°C. are represented graphically in Fig. 5.

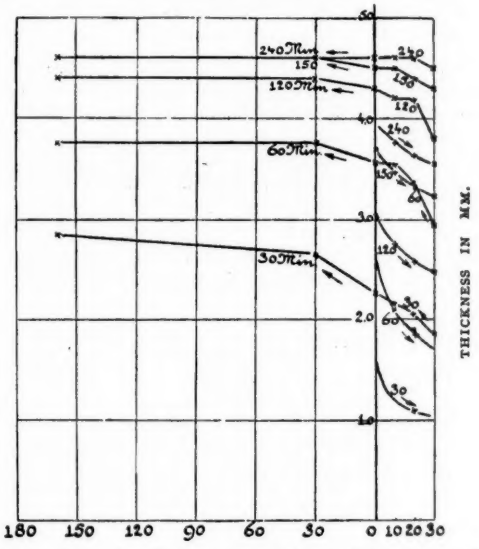

Fig. 5—Time in Minutes. Elasticity and Plasticity of Vulcanized Rubber at 147°C.

As with unvulcanized rubber, three properties of the vulcanized rubber were distinguishable:

a. Elastic recovery, *i.e.*, an instantaneous recovery.

b. Elastic after-effect, *i.e.*, a slow recovery.

c. Plasticity, *i.e.*, the residual permanent compression.

These three properties have been expressed as percentages of the total compression after 30 min. pressure, and the values in per cent are shown in Table 3.

From these figures the following conclusions may be derived:

At 18°*C.* For short times of cure the vulcanized rubber shows elastic recovery, and elastic after-effect, with no plasticity. The elastic recovery increases rapidly with time of cure, being 100% for 150 and 240 min. cure.

At 100°*C.* Undervulcanized rubber (30 min. cure) shows elastic recovery, some elastic after-effect and also a certain degree of plasticity, which diminishes to zero at longer times of cure. After 240 min. vulcanization the rubber shows only elastic recovery.

At 130°*C.* The vulcanized rubber has the same properties as at 100°C., though the undervulcanized rubber (30 min. cure) shows a larger percentage of elastic after-effect.

At 147°*C.* The relation between the properties has considerably changed.

The undervulcanized rubber shows a much smaller degree of elastic recovery and of elastic after-effect, and a larger plasticity. With increasing time of cure the elastic recovery increases to 65%, the elastic after-effect decreases to 7%, and the plasticity decreases slowly, but even after vulcanization for 240 min. is still 28%.

These figures prove that vulcanized rubber shows considerable

plasticity. In the case of undercured rubber, this is obvious even at 100°C., while rubbers cured for longer periods show considerable plasticity but only at 147°C. These considerations are important from a scientific as well as from a technical standpoint.

The foregoing results in regard to plasticity have been derived only from compression-recovery tests. It will be highly important to get a better insight into the elastic and plastic properties at high temperatures during elongation tests also. Only a thorough study of elasticity-plasticity relations under various conditions will give us eventually a real constructive view of the qualities of rubber.

It may be pointed out also that the experiments described above require to be coordinated with the results of X-ray tests of rubber under compression, as it is probable that the properties of rubber may be explained to a considerable extent from its X-ray spectrograms.

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Researches on the Structure of Rubber*

Paul Bary and Ernst A. Hauser

IN recent years studies of the properties of raw and vulcanized rubber have chiefly followed three lines of investigation, leading to a clearer conception of the structure of rubber.

(1) The existence of two components in rubber.

(2) The transformation of one of these components into the other.

(3) The structure indicated by diagrams obtained with x-rays.

At first it appears difficult to correlate the various observations, but after giving a resumé of the principal points, we shall propose a concept of the structure of rubber which explains its general properties and reconciles the older and the newer results.

In 1867 Govi[1] tried to explain the phenomenon today known as "the Joule effect," viz., that rubber becomes warm when elongated and cool when retracted, and if subjected to an elongating force, it contracts on heating. Govi considered rubber analogous to a solid foam, in which the spaces are filled by a gas. This theory was criticized by Thomas[2] in 1869 and later by Hesehus[3]. They determined the specific gravity of rubber and then dissolved it to permit any occluded gas to escape. After evaporating the solvent, they determined the specific gravity of the solid residue, and found the value identical to that which they obtained at first. In 1886 Malock[4] suggested the hypothesis that rubber is a mixture of an easily deformed substance and a rigid substance. A similar hypothesis, though more systematically developed, was suggested by Fessenden[5], who, basing his opinion on observations made with other substances, thought that rubber consisted of two substances, inelastic in themselves, which, however, being soluble in each other, could give under certain circumstances a mixture having elastic properties. According to Fessenden, rubber can be considered as formed of a mixture of a mass having little extensibility and a mass which is plastic. To render this hypothesis more intelligible, Fessenden made an interesting series of experiments, using hollow metal balls filled with water[6].

At the beginning of this century, new theories were advanced with progress in physical chemistry, depicting in a more profound way the internal structure of rubber. The work of Breuil[7] should be mentioned, his opinion being that rubber is formed of certain molecules imprisoned in a plastic medium, and that of Chaveau[8], who attributed the unusual properties of rubber to changes produced in the molecular arrangement, and to modifications which the inter-

*Translated from Revue générale du caoutchouc, June, 1928, pp. 3-11, by J. P. Fahy.

molecular spaces undergo. Similar theories were advanced by Schwartz and Kemp[9], and by Chéveneau and Heim[10], who considered rubber as formed of hard, inelastic kernels surrounded by a deformable, very elastic substance. Weber[11], and afterwards Caspari[12], were without doubt the first to try to prove experimentally that rubber consists of two hydrocarbons entirely different in physical properties. Though this assumption has been frequently criticised, Duclaux[13], Feuchter[14], and later Pummerer[15] succeeded in fractionating rubber into two hydrocarbons of different physical properties. Paticularly in the last few years when interest has been awakened in the source of rubber, that is, latex, a large number of studies have been published on the structure of rubber. Those of Pickles[16], Lunn[17], Freundlich and Hauser[18], van Rossem[19], Park[20], and Hauser[21] particularly should be mentioned. These publications are all based more or less on the character which rubber would possess if it contained two distinct phases, as have been shown by means of the micromanipulator really to exist in the particles of *Hevea braziliensis* latex.

From the first it has been considered necessary to explain the physical properties of whole rubber by the existence of two components which differ only in their physical properties and which have the same empirical formula $(C_5H_8)n$. The truth of this assumption has been proved by the numerous authors whose works have just been mentioned. In this paper these two forms of rubber will be called α-rubber and β-rubber, the former indicating the more soluble rubber of Feuchter[22] and the latter the less soluble.

The Change of α-Rubber to β-Rubber and Vice Versa

The chemical generalization that the fusibility, solubility, and volatility of polymers decrease with increase in the degree of polymerization immediately suggests the thought that the two forms of rubber differ only in their degree of polymerization, α-rubber having smaller molecules than β-rubber.

The fact that rubber softens with increase in temperature, passing from a solid to an almost liquid state but only in progressive stages and over a considerable range of temperature, suggests a transformation by heat of β-rubber into α-rubber, the increased mobility being due to a reduction in size of the molecules. On cooling, the opposite phenomenon takes place slowly, but the plasticity of the rubber does not follow the variations in temperature closely, for the greater the viscosity, the slower is the rate of re-polymerization.

The theory of varying degrees of polymerization in rubber is based on a long series of observations of the most varied nature, and permits the explanation and prediction of what will happen in the most diverse cases. Thus it would be expected that milling rubber in the cold greatly reduces its average degree of polymerization, since its solubility increases with this treatment; the same reduction obtained by heat produces the same effects. The proof that dissolution of rubber is accompanied by a diminution in the average degree of polymerization of the molecules is shown by the fact that rubber that is milled or heated for a long time and thus rendered plastic, dissolves more readily and completely than similar rubber not subjected to such treatment.

The viscosity of solutions of rubber which has been milled or heated is in general much less than that of solutions of the same rubber not so treated. A recent work of Fry and Porritt[23] shows the importance attached to this property in following the variation in the degree of depolymerization of rubber under various influences.

The action of heat and of mixing on the solutions themselves changes the viscosity to a greater or less degree, as shown by Caspari[24], Axelrod[25], Fol[26], and Klein and Stammberger[27].

Heat and mechanical treatment, which change the solubility of rubber and give its solutions different properties, can only be interpreted by assuming a reduction in the degree of polymerization, with increase in solvation, which is considered in itself as a chemical reaction.

Other weak chemical reactions, such as oxidation or vulcanization, are accelerated in the same way as the solubility, and by the same means (heating, mixing, or previous solution).

Resins dissolved in natural raw rubber and combined with it in the form of solvates give to the product properties similar to those of solutions made from rubber which has been heated or milled. In particular the viscosities of such solutions are very low compared with those of rubber from which the resins have been previously extracted, as shown by Fol[28] and Stevens[29].

All these facts are well known, as they have been studied as much from a practical point of view as by scientific experiments, and there is no need to dwell on them longer.

On the other hand it is known that rubber which has been mixed or which has been recovered from solution by coagulation or evaporation, when left for a sufficiently long time in darkness at a slightly elevated temperature, regains its initial properties and "nerve," and can even harden completely. In this case there is an increase in the degree of polymerization, or a more or less complete return to the original condition.

The sum total of these results has already led one of us[30] to express the opinion that the hydrocarbons, α and β, of which rubber is composed are associated after the manner of the two components of a jelly.

The experiments of Bary and Fleurent[31] have shown that rubber whose state of polymerization has been disturbed by mechanical working or heat can be modified either by increasing the quantity of α-rubber and decreasing the β-rubber, or vice versa.

From these facts it follows that the α- and β-forms of rubber are essentially transformable one into the other, but in any case the ratio α/β tends toward an equilibrium which is more or less rapidly attained[32].

The Number of Phases in the System "Rubber"

The fact that two analogous but different components exist in rubber can be considered as absolutely established, but the manner in which they are united is not so clear.

If, as we think, rubber can be considered as a jelly, that is, if the system can be regarded as the solution of two or more polymers of rubber in each other, then it is similar to a solution of crystalloids in water or in a mixture of other liquids, and the system, no matter how many components it contains, will comprise but a single phase[33]. Such a system is optically empty, that is, absolutely transparent.

The purer a rubber is the more closely does it fulfill this last condition, but it is never perfectly transparent, for in no case can it be considered as perfectly pure. Nevertheless, it may be assumed that, if complete purification were possible, an optically empty system would be obtained.

Granting this conception, rubber is representative of the class of substances defined by Wo. Ostwald as *isocolloids*, that is intimate mixtures of the same substance in different degrees of aggregation.

However, rubber is considered by Ostwald[34] as formed by the dispersion of β-rubber in a continuous medium of α-rubber while in the hypothesis of solid solution and the existence of a single phase, the mixture of the α- and β-forms has the structure of a solid (β-rubber), swollen by a liquid (α-rubber) in the same way that gelatin can be swollen in water.

The difference between these views is based upon the mechanical properties which one can expect of the two systems.

If a fine powder is mixed into a liquid or pasty substance such as α-rubber, the fluidity of the liquid or paste is diminished, and a more or less plastic mass is obtained, but the liquid or paste is never transformed into an elastic solid. To obtain the latter, the solid part of the mixture must possess a strong intermolecular cohesion, which is conceivable only if the molecules are in a dispersed state, either alone or in aggregates.

The same characteristics are observed when a jelly (obtained by swelling a hydrophilic substance) is compared with a gel, such as that produced in the formation of a colloidal substance by the separation of the liquid medium. The first case corresponds to a state of affinity of the colloidal substance for the liquid which it absorbs, while the second is, on the contrary, a syneresis and expulsion of liquid previously held in union.

A *jelly* is a one-phase system, and we have shown[35] that swelling is accompanied by the chemical phenomena of depolymerization and solvation. A *gel* on the other hand contains two or more phases, whatever may be the state of dispersion of any one in the others.

X-Ray Diffraction Spectra

In 1925 Katz and Bing[36] observed that when examined by x-rays rubber under tension gives a diagram which is identical with the diagrams of different kinds of fibrous substances. When not under tension, rubber gives only one or two faint amorphous rings[37]. This observation has lately been very useful in researches on the structure of rubber. From the first it was agreed that this mode of experimentation was the only practical means of approaching the study of the structure, and such success has been obtained that we may hope for future progress in fields of research which are unknown at present.

A large part of our knowledge can be credited to researches with x-rays, and special attention should be given the work pursued in this direction. Katz[38] has also observed in a later work that the interference spots become visible only when the rubber is elongated 80 to 100%, and he was able to prove that they disappear when the tension is released or when the rubber is heated. We also owe to him the first observation that vulcanized rubber gives a similar diagram when it is stretched, with the sole difference that the intensity of the interference spots is a great deal weaker than in the case of raw rubber.

Hauser and Mark[39] have studied these phenomena systematically and have made the first important contribution in this field of research, a field which has since been greatly developed. They confirmed the observation that the interferences appear only at a minimum elongation of 80 to 100%, and they also proved quantitatively that these interferences do not change from the moment of their appearance up to a maximum elongation of about 1000%, but that their intensity does increase proportionally to the degree of elongation. These researches were made by comparative measurements with a precise photometric standard. Moreover it has been established that the position of the amorphous band does not vary, but that its intensity decreases almost in proportion to the increase in elongation. The experiments were also carried out on rubber under tension in

two directions, in all directions in a single plane, and also on rubber under compression, the resulting changes in the diagrams being examined. In all cases the results absolutely agreed with those which would be expected of a purely crystalline structure. In every case of a rubber under tension it has been possible to establish an anisotropic structure identical to the fibrous ring diagrams of Weissenberg, rubber under torsion giving a fibrous diagram of the spiral type.

The same authors have tried to explain the appearance of the interference spots, as is done for other substances by the theory of normal crystals. They succeeded completely by assuming an orthorhombic, rectangular crystalline system with the long axes parallel to the direction of stretch ($a = 7.68$ A.U.)[40], while the other two axes are 8.0 and 8.6 A.U. respectively. Under these conditions the molecule of the elementary substance should be represented by $(C_5H_8)_4$, though in the case of highly stretched samples a double formula should be assumed, *i.e.*, $(C_5H_8)_8$. To produce these interference spots it is necessary to employ samples which are greatly elongated.

In explaining the results, Katz on the one hand, and Hauser and Mark on the other, differ in opinion in that Katz supposes a regular formation of crystals during elongation, while Hauser and Mark, basing their opinion on similar researches with organic compounds, think that the "crystallization" which causes the interferences to appear during the elongation already exists in the non-elongated substance in the form of aggregates of molecules. Granting this hypothesis, which is the basis of the well-known theory of these authors, one is led to consider the crystallites as swollen by a non-crystallized portion when the rubber is at rest. The de-swelling produced on stretching the sample is then the cause of the interference spots. From the mean value of the maximum intensity of the interference spots, Hauser and Mark have been led to conclude that the dimension of the particles need not change during the elongation and that the increase in intensity is due to the continuous appearance of new crystallites of equal dimensions.

Katz and several other investigators had already observed that rubber may give a Debye-Scherrer diagram without being under tension, with unaltered interference spots. The appearance of a Debye-Scherrer diagram, in which the simple bands correspond to the position which the interferences normally occupy under exactly similar experimental conditions, leads to the conclusion that the crystallites must already be present in the material before elongation but that they are not oriented. This observation quite agrees with the preëxistence idea accepted by Hauser and Mark. From the point of view of rubber technology, its interpretation is rendered rather difficult by lack of sufficient data on the samples employed. It was only after a complete study that it was possible to show that raw rubber, which has become hard and inelastic after long storage (in the state called "frozen rubber" by the rubber industry), shows the same Debye-Scherrer bands, which seem to explain this phenomenon also[41]. By analogy with numerous determinations made with natural colloids, it may be assumed that on storing certain changes occur which are known as "aging" and which are due generally to a contraction of the skeleton structure. The arrangement of the interference spots in the case of rubber which has not been stretched seems to be due to the fact that during its manufacture the rubber has undergone elongation effects which harden it for a rather long time. If such a hardened rubber is rapidly stretched or heated several times, it regains its elasticity and simultaneously loses its property of giving interferences without being previously stretched. Here again is a completely isotropic substance. This effect is most

extreme in the case of rubber subjected to repeated adiabatic elongation, which is called "racked" rubber[42]. It is possible under these conditions to obtain samples racked from smoked sheets with an elongation of 10,000% and more. This rubber has not only a sheen or silky appearance but shows very marked differences from normal rubber. Racked rubber is practically inelastic and resists tension like natural fibres. Examination with x-rays has also shown characteristic differences from normal rubber. If the rubber has been racked to the maximum, it shows a certain number of entirely new interference spots, which can probably be interpreted by introducing into the calculation a multiple of the factor 4 given above. Moreover the amorphous band entirely disappears. Probably then under these conditions the orientation of the rubber is complete, or in other words maximum de-swelling is reached.

Experiments made with other organic substances which thus far have failed to give interferences with x-rays should also be mentioned. Meta-styrol deserves special attention in that it shows an amorphous band very similar to that of rubber. If this substance is racked, Hünemörder[43] has shown that at an elongation of about 1000% distinct signs of interferences in the equatorial line become evident. It may be assumed therefore that, were this substance strongly racked, a complete fibrous diagram would be obtained. The only reason that this experiment has not been carried out is that certain experimental difficulties have thus far not been solved.

Interpreting the Diagrams

A point regarding the structure of rubber which is not sufficiently explained is that mentioned above; *viz.*, that interferences appear only at elongations of 80 to 100%. However, recent researches on the effect of the speed of elongation on the resistance to extension seem to throw new light on this question. It has been shown that the stress-strain curves of raw rubber depend not only on the speed of elongation but also on the temperature at which the experiments are carried out. It has been possible by employing very slow speeds and high temperatures to obtain elongation effects showing differences from those obtained under normal conditions. In the case of these researches, which have been discussed in detail by Hauser, Rosbaud[44] and Schmid[45], it has been possible to show a flow similar to that already known to take place in the case of metals.

In view of these established facts, it has seemed equally interesting to study with the aid of x-rays very slow elongations, and thus it has been shown that, although raw rubber gives a distinct diagram at 500% elongation, it shows only an amorphous band at the same elongation if the tension is applied slowly[46]. In other words the rubber remains isotropic, as can be seen under the microscope, and the sample remains clear. All the results obtained lead to the conclusion that this effect is a result of a flow or displacement of the substance and that the speed of de-swelling is exceeded by the speed of flow. However, it seems justifiable to put a more precise limitation on the minimum elongation necessary to obtain the interference spots, *viz.*, 80 to 100%. However, it is not impossible to obtain the same effects with less elongation if the correct choice of speed and temperature are employed. It should not be forgotten that the time necessary to obtain the x-ray diagrams is rather long, and it must be admitted that at low elongations the flow effect is the greater, and consequently the interferences cannot be visible. Hauser and Mark, after having accustomed their eyes to the dark, have been able to show many times by employing a fluorescent screen that the appearance of the interferences is a spontaneous effect, and that consequently it seems possible that the

interferences can be likewise observed at very low elongations if the proper speed and temperature are chosen.

In recent literature, it is frequently noticed that the results of researches with x-rays and those obtained by microscopical examination of latex have been confused and inexact suppositions have been made by comparing the special structure of the latex particle with the results obtained with x-rays. If the difference in size of the objects studied in the two cases is considered, it is clear that this confusion would not occur. Rubber that has been milled until the latex particles are completely destroyed regains its elasticity on vulcanization, and on elongation gives an x-ray diagram. The same rubber, if well broken down and then let stand for a long time, shows the typical Debye-Scherrer band already mentioned. Moreover, by proceeding with the greatest care, by dissolving in ether, so-called "total rubber" or chemically pure rubber can be separated, and though the latter may be formed of several fractions giving exactly the same diagram, the hypothesis seems correct, since the least soluble fraction gives the greatest effects, and that substance ought to predominate when the interferences are observed.

X-ray diagrams obtained in the study of raw rubber when it is not elongated, when it is elongated, or when it is in the form called "frozen," have shown as already said, either amorphous bands in the first case, or well defined interference spots giving the appearance of a fiber diagram in the second case, or finally Debye-Scherrer-Hull rings in the third case. It appears interesting to discuss briefly the information that can be obtained from these three distinct effects obtained with monochromatic x-rays. In all cases a beam of monochromatic x-rays was employed, and the pictures were taken by placing a photographic plate or film at a right angle to the incident beam behind the material under examination. Accordingly this method can be compared with that employed by Laue in the examination of crystallographic lattices.

According to the theory of Bravais, the atoms or molecules in a given crystal are systematically arranged in a definite lattice, and thus maximum interferences result. In an amorphous substance as for example a liquid, the atoms or molecules have no regular arrangement in the lattice any more than they can be considered as placed in parallel equidistant planes scattered about by chance. Consequently the diffraction obtained with these substances produces a general blackening of the plate, or, as usually happens, a large diffuse band in the immediate vicinity of the primary incident beam. This diffuse band, observed in non-elongated rubber and also in liquids, glasses, jellies, etc., is easy to distinguish from the picture given by a crystal, and even from the interferences given by colloidal crystalline particles. In some cases, however, particularly with rubber that has been "frozen" by long storage until it has become hard and opaque, x-rays give concentric continuous rings (Debye-Scherrer-Hull) if the rubber has not been elongated. These rings are likewise obtained in the study of powdered crystals. The appearance of these rings indicates, in the case of rubber, an accidental formation of a reticular structure, or a diffraction produced by atoms regularly spaced in molecules distributed by chance, that is, the formation of molecular aggregates or of fragments of crystals, with no definite orientation.

Doubtless the most important effect is that obtained by elongation. If a sample of "frozen" rubber is elongated, there is obtained, besides the amorphous ring or the Debye-Scherrer-Hull rings, definite interference spots which become clearer the greater the elongation. At the same time the amorphous band or the Debye-Scherrer-Hull rings decrease in intensity and lose more or less of their continuity. The interference spots, however, as already said, keep their position. A pure, fibre diagram with spots which

are located on branches of hyperbolas is then obtained. This leads to the conclusion that a material is involved which produces a diffraction like crystals arranged parallel to the direction of the force applied. The accuracy of this statement is based on the fact that the spots are located on hyperbolas as in the case of perfect fibres. All evidence seems to show that true crystals do not exist in rubber before elongation, but that it contains molecular aggregates of definite dimensions (micelles), which do not give interference spots for a reason similar to that which produces this result in the case of crystals which have been heated to a high temperature. The primary particles have an amplitude of oscillation too great for any distinct interference to be obtained. During the elongation, the interior orientation becomes more regular and interference points appear. As the position remains constant and as only the intensity increases, and as the size of the line of diffraction does not change, it must be assumed that the crystalline units do not increase, but that new units appear.

From the results obtained by different experimental methods the following conclusions are warranted regarding the nature of rubber, which may contribute to an explanation of its properties.

1. There exist two components or two types of components with the same elementary chemical constitution, but of differing degrees of polymerization and very different degrees of fluidity. The type of component with the greater degree of fluidity naturally corresponds to hydrocarbons having the lower state of polymerization.

2. The relative quantities of the two components of rubber vary in such a way that calling α and β the average values for the degree of polymerization of each of the components, and n_1 and n_2 the number of corresponding molecules, the ratio $\frac{n_1\alpha}{n_2\beta}$ varies particularly with the temperature and various mechanical treatments.

3. At ordinary temperature or at somewhat lower temperatures, rubber at rest tends toward a very low value for the ratio $\frac{n_1\alpha}{n_2\beta}$ which is increased by work or heat or by repeated elongations.

4. The fact that unstretched "frozen" rubber which has been stored at a low temperature gives the Debye-Scherrer-Hull rings when the quantity of β-rubber has increased at the expense of the quantity of α-rubber shows that it is the less diffusible form of rubber which gives the Debye-Scherrer-Hull diagram.

5. In the elongation of normal rubber (not frozen) the α-component, which was dissolved in the β-component to form a jelly, separates as a result of the negative internal pressure caused by the extension, and the jelly changes to a gel, that is, to a two-phase system.

6. In the elongation of "frozen" rubber there is a return to the normal form of "non-frozen" rubber, as there is on heating.

These results, based on experiment, indicate the presence in rubber of a sort of network of solid β-form which becomes on elongation a bundle of parallel filaments. Moreover, the reality of these filaments is confirmed by the "crystallization" experiments of Pummerer and Koch[47] and of Feuchter [48] and by the freezing of stretched rubber by Hock[49] and by microscopic observations on solutions of rubber during evaporation by Bary[50].

Conclusions

The theory according to which rubber consists of two components which normally are dissolved one in the other (Bary), is based on a number of physico-chemical observations, and is in general agreement with the results of x-ray work.

The very nature of the x-ray diagrams substantiates the theory by introducing the idea that stretching rubber causes a separation

of part of the dissolved component from its solvent (theory of Hauser and Mark).

It may be concluded that rubber consists of a network of β-rubber which is capable of giving x-ray diagrams only when it is sufficiently condensed, that is, when its chains of carbon atoms have little freedom of oscillation. This result can be obtained either by freezing the rubber, which increases the proportion of the β-form, or by elongation, which expels the α-portion and concentrates the β-portion.

This concept appears to explain all observations on the physical and mechanical properties of rubber.

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A Scheme for Accelerator Classification

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MUCH has been written about the constitution and chemical behavior of vulcanization accelerators. Theories have been advanced regarding the mechanism of vulcanization effected with their aid. Yet even the authors of such papers—presumably best qualified to interpret their contents—would hesitate to predict, from chemical structure, many of those features which are of practical interest to the rubber manufacturer. Nevertheless, an increasing number and variety of organic accelerators are being offered on the market, and it is not strange that the mind of the average rubber man is confused by the excess at his command and the conflicting claims of the distributors. In these circumstances it is natural to hesitate to undertake the somewhat formidable task of sorting and classifying.

Fortunately, however, it is not necessary to do all the work of classification on a factory scale. Certain laboratory helps are available and can be used to reduce considerably the arduousness of the task.

It is believed that an outline of such methods, a discussion of their significance, and a table of results, may be helpful to many in the industry, and it is for this purpose that this paper has been written.

For the sake of brevity, we have tabulated the accelerators by classes, where possible, rather than by individual compounds. Our classification is as follows:—(1) *Dithiocarbamates*, represented by such accelerators as Vulcacit-P, Superac and Grasselerator 552. This also includes the metallic salt of dithiocarbamic acid such as the Supersulfurs Nos. 1 and 2. (2) *Xanthates*, zinc salts of ethyl, propyl and butyl xanthic acid. (3) *Thiurams*, these include tetramethylthiuram mono- and disulfides. (4) *Mercaptobenzothiazoles*, including metallic and amine salts. (5) *Vulcanol*, not a class. (6) *Faster Aldehyde Amine Derivatives*, such as A-16 and A-20, B. B., Grasselerators 808 and 833, Heptene. (7) *Paranitrosodimethylaniline*, not a class. (8) *Ethylidene Anilines*, A-7, A-19, Crylene, R & H-40 & 50, Tensilac 39 & 41, Vulcanex, Vulcone. (9) *Aldehyde Ammonia*, not a class. (10) *Guanidines*, such as diphenyl and di-ortho-tolyl, phenyl-ortho-tolyl and triphenyl guanidines. Triphenyl and tri-ortho-tolyl guanidines differ in speed and strength from properties listed in the table. (11) *Hexamethylenetetramine*, not a class. (12) *Thioureas*, diphenyl, di-ortho-tolyl and di-meta-xylyl thioureas.

In Table 1, various accelerator properties have been listed in the

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TABLE 1—ACCELERATOR CLASSIFICATION

	Speed at 40-60 lb. per sq. in.	Speed at 5-30 lb. per sq. in.	Handling Scorch	Handling Softening	Sulfur	No Stiff	Load Ten.	Blk. Stiff	Load Ten.	Persis. during cure	Antiox. Prop.	Stiff. after Vulc.	Air cures	Stearic acid in ext. rubber
Dithiocarbamates	1	1	2	No	Low	High	High	High	High	Fugitive	None	Yes	O.K.	Unnecessary
Xanthates	N.G.	1	1	No	Both	High	High	High	High	Fugitive	None	Yes	O.K.	Required for high mod. & tens.
Thiurams	2	2	3	No	Low	High	High	High	High	Fugitive	Fair	Yes	O.K.	Unnecessary
Mercaptobenzothiazoles														
Captax	3	3	6	No	Low	Low	Low	High	High	Pers.	Good	Yes	O.K.	Required
Z-88	3	3	5	Yes	Low	High	High	High	High	Pers.	†Fair	Yes	O.K.	Required
W-80	3	3	5	No	Low	High	High	High	High	Pers.	Fair	Yes	O.K.	Required
Vulcanol	4	4	7	Yes	Low	High	High	N.G.	N.G.	Pers.	Fair	Some	—	Unnecessary
Faster aldehyde amine Derivatives	4	4	8	Yes	Low or med.	High except heptene	med.	Vary poor to low	From poor to good	Pers.	Vary, some *fair	Some	Fair cure	Need very little
p-nitrosodimethylaniline	4	4	5	Yes	Med.	High	High	Fair	Good	Pers.	Good	Yes	O.K.	Required, but needs no ZnO in reg. rubber
Ethylidene anilines	5	5	9	Yes	Low or med.	Low	Low	Mostly Low	Fair	Pers.	*Fair	No	Fair cure	Need very little
Aldehyde ammonia	5	5	10	No	Med.	Low	Low	Fair	Fair	Pers.	None	No	No cure	Unnecessary
Guanidines	6	7	11	No	Low or med.	High	High	High	High	Pers.	None	No	Poor cure	Need very little
Hexa	7	N.G.	12	No	Med.	High	High	High	High	Pers.	None	No	No cure	Required except with high ZnO
Thioureas	8	6	4	No	High	Low	Low	Fair	Low	Pers.	Poor	Yes	O.K.	Cures without stearic in high ZnO, but no set cure

*Longer cures and higher temperatures change accel. to sulfur reaction prod. which is not antioxidant. †Proportional to thiazole content.

approximate order of their interest to a prospective user. Speed and scorching tendencies have been given a numerical classification, increasing numbers indicating decreasing activity. Other comparisons are indicated in qualitative terms, the basis for which will be explained later in the paper. The terms "No Load" and "Blk Load" refer to compounds containing no pigment loading and carbon black loading respectively. The sub-classes refer to the stress-strain stiffness and the tensile strength produced by the various accelerators in these mixings. The other headings are self-explanatory.

Table 2 is a list of some of the more common commercial accelerators with their chemical names.

When a rubber manufacturer questions the suitability of an accelerator for his purposes, he is in reality seeking an answer to some or all of the following questions:—(1) *Speed.* Does it work best at high temperatures (40 to 60 lbs. per sq. in.) or at low temperatures (5 to 30 lbs. per sq. in.) and how does the speed at high and low temperatures compare with other well-known accelerators? (2) *Handling.* What are its scorching tendencies at handling temperatures? Does it soften rubber? Does it disperse readily? (3) Does it work best with high or low sulfur? (4) *Non-loaded stocks.* Does it give high stiffness and tensile strength in stocks without pigment loading? (5) *Carbon Black Mixes.* Does it give high or low stiffness and tensile in carbon black stocks? (6) Is it persistent during cure? (7) Does it have antioxidant properties? (8) Do its vulcanizates stiffen upon aging? (9) Is it suitable for air cures? How does its rate of cure in open steam compare with mold cure? (10) Does it require stearic acid? (11) Is it stable in uncured stock or does it lose strength?

It will be noticed that some phase of curing is involved in nearly all of these questions. It is obvious that if comparisons are to be made with other accelerators, or, in fact, for various ratios of a given accelerator, comparable conditions must be observed, and especially where stress-strain properties are to be compared, comparable states of cure should be obtained.

Elsewhere (*Ind. Eng. Chem.*, **18**, 145, 1926), the disagreement among rubber technologists, as to cure criteria, has been referred to, but the method, in brief, is to select as the optimum of a series of cures, that cure for which natural aging produces the least change in physical properties. This cure has been found, by experience, to be the one offering the greatest resistance to hand tear.

The table of accelerator properties herein presented has been prepared by the use of the hand tear criterion. It should be pointed out that the selection of some other standard may considerably affect the arrangement of accelerators. In support of this conclusion it may be of interest to present a summary of some recent data collected by Dinsmore and Zimmerman.

Since the time for reconciliation of the conflicting ideas regarding cure criteria is apparently remote, it seemed that a useful purpose might be served by comparing several of the methods in stocks of different types.

In order to throw more light on this matter, mixings with four different kinds of loading were prepared, each cured with four different curing agents. These were further tested in three different plantation rubbers. Ten parts by weight of sulfur on one hundred of rubber was adopted for all unaccelerated cures. The accelerated mixings were adjusted to best cure of approximately 60 min. at 40 lbs. per sq. in. (as judged by hand tear) for hexa-

methylenetetramine and diphenylguanidine, and 60 min. at 20 lbs. per sq. in. for mercaptobenzothiazole, using a blended batch of

TABLE 2. COMMERCIAL ACCELERATORS.

A-7	Same as Ethylidene aniline. Soft.
A-11	Same as Vulcone.
A-16	An aldehyde amine.
A-19	Same as Vulcone.
A-20	An aldehyde amine liquid.
Aero-X Ami	Aniline di-isopropyl dithiophosphate.
Aldehyde ammonia	Chemical name.
B.B.	Para-aminodimethylanilinebutyraldehyde deriv.
Captax	Mercaptobenzothiazole.
Crylene, hard form	Same as Vulcone.
" paste	" " " with stearic acid.
Di-ortho-tolylguanidine	Chemical name.
Diphenylguanidine	" "
Ethylidine aniline	Similar to Vulcone, but soft.
Formaldehydeaniline	Chemical name.
Grasselerator 102	Hexamethylenetetramine.
552	Piperidine piperidyldithiocarbamate.
808	Butyraldehyde aniline.
833	Similar to 808, but faster.
Heptene	Heptaldehyde aniline.
Hexamethylenetetramine	Chemical name.
Lithex	Like Super-sulfur No. 2.
Methylenedianiline	Methylenediphenyldiamine.
Monex	Tetramethylthiurammonosulphide.
No. 999 lead oleate	Chemical name.
Phenyl ortho-tolyl guanidine	" "
Piperidine piperidyldithiocarbamate	" "
R. & H. 40	Ethylidene aniline. Soft.
50	Same as Vulcone. Hard.
Safex	Dinitrophenyldimethyldithiocarbamate.
Super-sulfur, No. 1	Zn salt dimethyldithiocarbamic acid; clay base.
No. 2	b salt dimethyldithiocarbamic acid; clay base.
Tensilac No. 39	Ethylidene aniline. Soft.
No. 41	Same as Vulcone.
Thionex	Monex.
Thiocarbanilide	Chemical name.
Trimene base	Triethyl trimethylenetriamine.
Triphenylguanidine	Chemical name.
Tuads	Tetramethylthiuramdisulphide.
Vulcanox	-toluidine, modified Vulcone.
Vulcanol	CS_2 reaction prod. of butyraldehyde aniline.
Vulcone	Similar to ethylidene aniline, but hard.
W-80	D.P.G. salt Captax.
Z-88	Essentially NH_3 salt of Captax plus softener.
Zimate	Zinc salt of dimethyldithiocarbamic acid.
Zinc butyl xanthate	Chemical name.

rubber. The various rubbers, of course, varied this time of cure considerably. The proportions of ingredients used are shown in table 3.

TABLE 3.

LOADING ON 100 VOLUMES OF RUBBER	CURING INGREDIENTS LBS. PER 100 PARTS OF RUBBER						
	Sulfur only	*Mercapto		D.P.G.		Hexa.	
		Sul.	Accel.	Sul.	Accel.	Sul.	Accel.
(1) No loading (1 vol. zinc)	10.0	3.20	0.35	3.00	0.30	3.00	1.00
(2) 20 vol. ZnO	10.0	4.00	0.50	3.50	0.75	3.00	1.35
(3) 20 vol. carbon black	10.0	3.50	1.50	2.75	1.30	4.00	1.75
(4) 20 vol. car. blk. plus 20 vol. whole-tire reclaim	10.0	3.50	1.00	2.75	0.75	4.00	1.25

*Note—Mercaptobenzothiazole batches contained 2 parts stearic acid.

The smoked sheet used was considered the fastest of the three rubbers, the brown crepe next and the pale crepe slowest.

The mixings were prepared and tested as outlined in a previous article. Detailed test data are omitted for the sake of brevity and it has been thought sufficient to present a few curves showing the relation between cure optima selected by the more or less popular tensile-product method and by our hand tear method. A rather complete discussion of other methods as applied to unloaded stocks, occurs in our former article, and, as will appear later, discrepancies for loaded stocks, are small.

Figure 1 shows the time of best cure in minutes, as selected by both hand tear and maximum tensile product for three rubbers and four different loadings, cured with sulfur only. Figure 2 gives the same data for mercaptobenzothiazole acceleration. Figures 3 and 4 show respectively diphenylguanidine and hexamethylenetetramine acceleration.

An examination of Fig. 1 discloses the fact that there is a wide divergence between the optima selected by hand tear and tensile product for the unloaded stocks. This difference is reduced by the addition of 20 volumes of zinc oxide for, whereas the effect as judged by tensile product is to speed up the cure, the hand tear shows an actual slowing down. Carbon black behaves about the same as zinc oxide and the addition of reclaim accelerates the cure considerably, bringing the results, by both criteria, close together.

Figure 2 shows a much closer harmony between the two criteria, in fact, the only divergence is in the unloaded stocks.

Figure 3 shows the same as Fig. 2. The relative positions of the rubbers are reversed by the different methods, for unloaded stocks. The graphs for the loaded stocks are close as before.

Figure 4 shows a similar tendency with somewhat more difference in the unloaded stocks, when judged by the two criteria.

Although carbon black and zinc oxide exert the same effect on cure in the sulfur stocks, in accelerated stocks it was necessary to increase greatly the accelerator in the presence of black to approximate the time of cure of the zinc stocks. This shows that the carbon black exerts its greatest effect on the accelerator. It is also apparent that the sulfur mix with reclaim and black is almost as fast as the mixes with rather high accelerator content and lower sulfur. This would indicate a strong influence exerted by high sulfur on reclaim vulcanization.

To summarize the application of these results to the original problem, it is found that in unloaded stocks, especially when cured only with sulfur, but also when cured with accelerators, the discrepancy between optima selected by hand tear and tensile product is great. The hand tear method places best cure at a much lower time than maximum tensile product. The relationship between the speeds of various rubbers is also frequently changed by change in criteria. For loaded stocks, of the type tested, however, both methods agree fairly well. Hence it would seem that those differences of opinion which arise as to proper cure criteria may well be limited to the field of unloaded compounds.

It must now be obvious that, for unloaded stocks, the selection of a cure criterion has an important effect upon the relationship of accelerators as shown in our table.

It may perhaps be well to say a word of warning about a method of comparison which has found considerable favor in the past, particularly among accelerator vendors. It is based on the indisputable fact, that, by proper selection of the proportions of sulfur and ac-

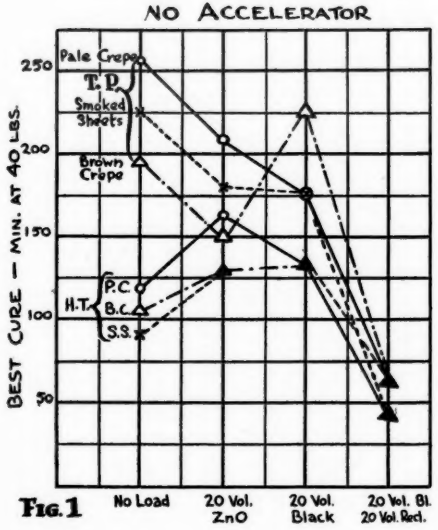

FIG. 1

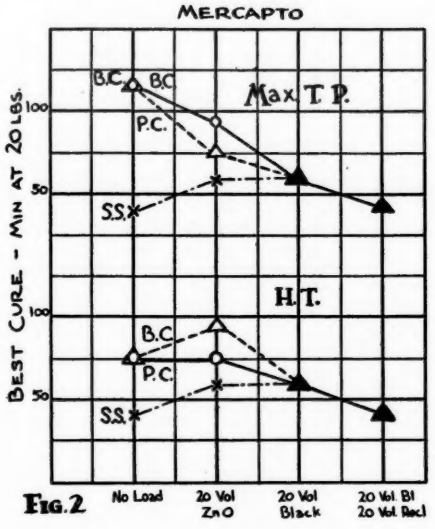

FIG. 2

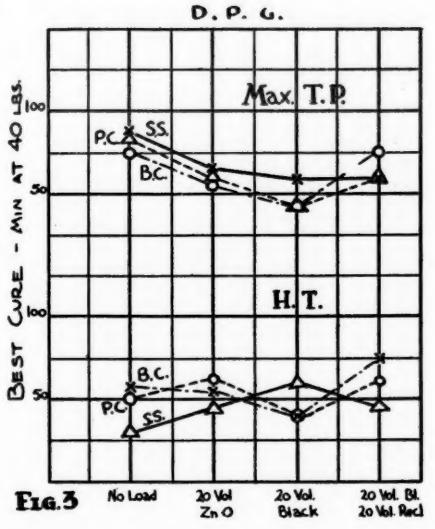

FIG. 3

celerator, most accelerators can be made to produce a flat tensile-cure curve. That is, the tensile rises to a maximum as time of cure increases, and the tensile then stays constant or drops but slightly for a considerable period. Many consider that the flat region represents satisfactory cure and that the curing ratios selected are, more or less, ideal and form a basis for comparing the value of accelerators. Lest there be any misunderstanding, let it be said here, that acceptance of the substantial equality of hand tear and maximum tensile product as cure criteria, does not involve the admission that prolongation of the tensile product for a further period, indicates concomitant prolongation of good aging properties. Some data may be of interest.

Figure 5 gives a representative result of the aging characteristics of a so-called "flat tensile" stock. For all practical purposes, the tensiles of the original cures are substantially constant from 30 to 120 minutes, which is a quite creditable flat curing range. The results of the aged stocks (6 days at 50° C. and 150 lbs. per sq. in. oxygen pressure) show that for cures longer than 60 minutes, the aging qualities are much poorer than for the shorter cures. It will be noted that the percentage-gain-in-weight curve increases linearly with respect to cure. These data are typical of an overwhelming mass of data which lead the authors to the conclusion that from the standpoint of the oxidation process, the rate of oxidation is a constantly increasing function of cure and bears no relation to the flatness of the curve showing the tensile strength and the time of cure, and as a result, that flatness of tensile strength over a range of cures means nothing at all from the point of view of the subsequent behavior of the stock on aging.

Having explained the position as to cure relationships, a consideration may be made of the individual question, propounded at the beginning.

1. *Speed*—This may be determined by trying both unloaded and loaded stocks with high and low sulfur at two temperatures, say 10 lbs. and 50 lbs. per sq. in. A range of cures at these temperatures will indicate a best cure for each. Four stocks will thus give an immediate rough classification. Further trials will be necessary to select the most suitable ratios.

Example:—

	Unloaded		Loaded	
	Low S	High S	Low S	High S
Rubber	100	100	100	100
ZnO (Vols. per 100 vol. R)	1	1	1	1
Gas Black or Clay (")	0	0	20	20
Sulfur (lbs. per 100 lbs. R)	3	6	3	6
Accelerator (")	1	1	2	2

Gas black and clay exert the greatest effect on cure. Most other pigments will take the same ratios as the unloaded stocks.

After best cures are selected for curing ratios which give best results, a comparison of the time and temperature of cure, together with amount of accelerator required, against a known accelerator, will enable one to classify the new accelerator, as to speed, fairly accurately.

2. *Scorching and its measurement.*—Well milled rubber is essentially a plastic and, when subjected to pressure (as in the Williams parallel plate plastometer) flows, and the flattened disc shows no change in dimensions on removal from the plastometer.

The softening effect of the accelerator on the rubber, which is generally very small or entirely non-existent, may be determined by this test. If, however, the rubber is not completely broken down or is scorched, then it possesses elastic properties. Hence, by imposing a pressure on such a sample, (*a*) plastic flow, (*b*) elastic deformation are produced. On removing such a sample from the

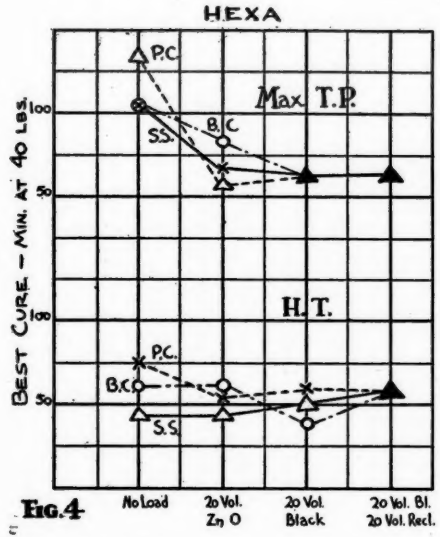

FIG. 4

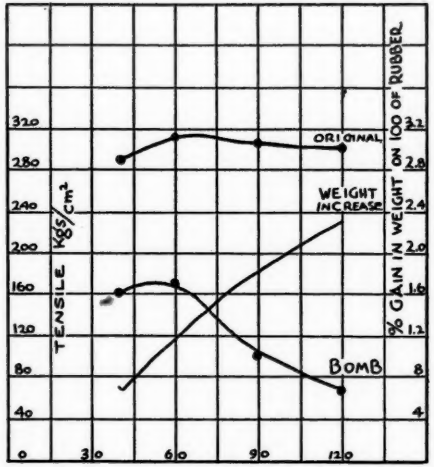

FIG 5

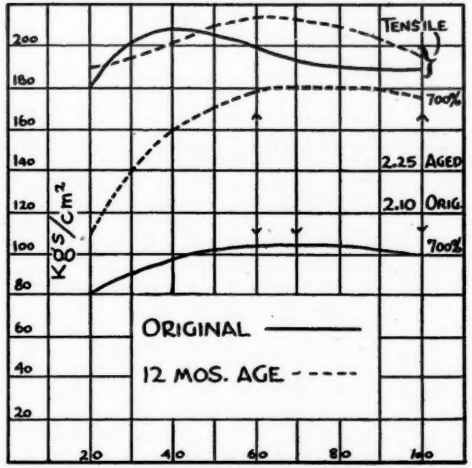

FIG. 6

plastometer, it will increase in thickness according to some function of its elastic properties. This recovery is taken by means of an ordinary thickness gauge after a definite time interval (usually 1 minute) after removal from the press. The difference between the reading so taken, and the final thickness of the sample, while under load in the plastometer, is taken as the recovery of scorch figure.* This method can be used to determine the scorching propensity of the accelerators by the following procedure. Samples of the raw stock (about 1 inch cubes) are heated in an air oven at 70° C., or, may be dropped into boiling water for increasing time intervals. The lower temperature of 70° C. gives a valuable forecast of the setting up or scorching of the stock in the liner or books after calendering, whereas the test in boiling water foretells whether the stock is liable to give burnt stock during the mixing operation. The usual 2 cc. pellets are then prepared from the so-treated samples, and tested for final thickness and recovery figure in the plastometer under the following conditions:—Temperature 70° C.; Load, 5 kgs.; Time, 3 mins.; Recovery taken 1 minute after removal from press. The thickness is recorded in millimeters and it is not necessary to figure the plasticity constant K as originally proposed by Williams.

A typical example of the results obtained by such procedure is given below.

Time of Heating at 70° C. in hours	Plasticity in mms.	Recovery in mms.
0	4.00	0.43
8	4.05	0.39
12	4.05	0.41
14	4.10	0.38
16	8.50	5.10

The abrupt change in properties between 14 and 16 hours is very striking, and furthermore allows of a rather exact determination of the relative scorching propensities. Of course, in many cases an inspection by tooth and thumb methods will suffice.

Dispersion—All powdered accelerators give better dispersion if mixed in master batches. Hexamethylenetetramine and the thioureas must be finely ground to give good dispersion.

3. *High and Low Sulfur.*—The work outlined under "Speed" automatically fixes the sulfur ratios, which may then be compared with those used for known materials. It need only be added here that some accelerators may require high sulfur for short, low temperature cures, and low sulfur for long, high temperature cures.

4. *Unloaded Mixes.*—The work on unloaded stocks, outlined under "Speed," forms the basis for this comparison. A stiffness figure, such as the load at 500 per cent elongation, is obtained at "best cure" together with the tensile strength. These may be classified, as compared with known standards, quantitatively, or qualitatively as "high" or "low."

5. *Carbon Black Mixes.*—The observations made under (4) apply here, except that, if the loaded stocks used in the speed test were not carbon black stocks, this work must be repeated with carbon black.

6. *Persistence During Cure.*—By this is meant the persistence of the curing influence of the accelerator during cure, as long as plenty of free sulfur is available. The accelerator may not remain in its original form, e.g., it may be transformed to its sulfur reaction product, but if its curing effect continues, it is said to be persistent.

*The exact method here outlined has been in use in the authors' laboratories for the past four years and has been successfully used to determine the degree of breakdown of raw rubber and uncured stocks, as well as degree of scorch of various milled batches.

This is in contradistinction to the fugitive type which ceases to exert curing effect as soon as it enters into the curing reaction and which is progressively exhausted.

Twiss and Thomas (*Jour. Soc. Chem. Ind.*, **42**, 499T, 1923; **44**, 100T, 1925), use certain characteristics of the stress-strain cure as criteria, whereas Hardman (*Ind. Eng. Chem.*, **19**, 1037, 1927) uses the combined sulfur figure. The method of Twiss and Thomas has been adopted as, in this study, the physical properties are of immediate concern. It may be, however, that in certain connections, the combined sulfur figure is more significant, e.g., consideration of ability of a vulcanized compound to resist heat, or, study of aging properties of overcured stocks. These points, however, can be independently determined.

7. *Antioxidant Properties.*—It has been shown (Bruson, Sebrell and Vogt) that Hevea rubber contains two or more so-called natural antioxidants, which are largely responsible for the protection of the rubber against oxidation. In order to study the antioxidant properties of accelerators, it seems most reasonable to do this in rubber stocks from which the natural antioxidant has been removed. Under these conditions, the aging properties of the accelerator can be evaluated independently, without the complicating effects

TABLE 4

					Tensile strength in kgs. per sq. cm.		Oxygen Bomb test 16 hrs. at 60° C.	
Accelerator	Amt.	Sulfur Amount	Cure mins.	lbs. per sq. in.	Original tensile strength	12 mos. tensile strength	tensile strength	% Gain in wt.
Captax	0.5	3.0	30	20	135	140	110	0.42
			50	"	145	150	110	0.57
			70	"	165	155	95	0.73
Vulcone	0.5	3.0	30	40	150	170	150	0.21
			50	"	165	170	50	0.63
			70	"	170	170	0	8.40
D.P.G.	0.5	4.0	30	40	160	155	0	14.4
			50	"	185	20	0	12.6
			70	"	195	20	0	12.1
"Hexa"	0.9	3.0	30	40	110	65	0	12.6
			50	"	145	90	0	13.0
			70	"	160	90	0	12.9
None	0.0	10.0	120	40	140	115	0	4.3
			150	"	155	75	0	3.8
			180	"	160	20	0	4.5
T.P.G.	1.0	6.0	50	40	145	70	0	9.7
			70	"	175	70	0	10.1
			90	"	185	75	0	10.7
"Thio"	2.5	6.0	50	40	125	145	0	2.8
			70	"	145	55	0	9.4
			90	"	155	20	0	11.0
Accelerene or p-nitroso dimethylaniline	0.5	3.0	20	40	105	135	125	0.20
			40	"	160	195	175	0.14
			60	"	170	210	170	0.13
Litharge	6.0	6.0	15	40	165	110	0	3.8
			30	"	180	105	0	10.0
			45	"	155	80	0	12.0

due to the natural antioxidant of the rubber. Therefore, by the simple expedient of extracting the crude rubber with acetone prior to its incorporation into the mix, the aging qualities of the cured stock are due almost entirely to the accelerator used in compounding the stock.

The important role that fatty acids play in vulcanization by accelerators has been sufficiently emphasized, so that it is evidently necessary to replace those removed by the extraction with acetone. Stearic or oleic acid in amounts of 1-2 per cent on the rubber supplies the necessary acid, and these materials have no antioxidant properties in themselves. Thus, batches consisting of 100 of acetone-

extracted rubber, 5 of zinc oxide, and 1.5 of stearic acid, to which appropriate amounts of sulfur and accelerator are added, are mixed and cured over a suitable range of cures. The cured sheets are then subjected to natural shelf aging or accelerated aging tests.

The Bierer-Davis bomb test offers a very rapid and exact means of evaluating the resistance of oxidation of the stocks under test. However, equally valuable results may be obtained by the Geer oven test. In this connection, the criterion of resistance to aging used by the authors has generally been that of tensile strength or product, but a very useful criterion is the percentage gain in weight which occurs on aging in the bomb. Results on a few representative accelerators are given in table 4.

The results show that Accelerene, Captax and Vulcone show definite antioxidant properties, particularly as revealed in the oxygen bomb tests, whether judged from the standpoint of tensile strength or weight increase. The 16-hour bomb test is more severe than 12 months natural shelf life.

8. *Stiffening after Vulcanization.*—This term is used to denote the increase in stiffness and sometimes also in tensile strength which takes place on aging. It may or may not be accompanied by any changes in the amount of combined sulfur. Figure 6 gives a graphic picture of the changes in physical properties and combined sulfur which occurred on natural aging for 12 months. The physical properties are represented by the load at 700 per cent elongation and the tensile strength of a range of cures, both in the original and after 12 months natural shelf aging. The original properties are virtually constant over the range of 20 to 100 mins., i.e., no further increase in stiffness can be obtained by further cure, yet by storage, the stiffness of all cures is almost doubled. The combined sulfur changes which have occurred during the aging period are insignificant. For instance, the 60 min. cure increases from 1.55 to 1.80 per cent. An original cure which would have a combined sulfur value of 1.80 per cent. would require a curing time of 70 mins. The resulting physical properties of such a cure would differ not at all from the 60 min. cure.

Hence one may say that the stiffening of the aged stock is practically independent of the increase in combined sulfur, or if it is dependent, then the very slightest increase in combined sulfur which takes place on aging exerts a tremendous effect on physical properties, which increase cannot possibly be obtained by very much larger increases occurring during the original curing period.

The point of interest in connection with accelerator evaluation is that this stiffening may be simulated by artificial aging tests which eliminate oxidation effects. The primary result of oxidation is to cause softening in its early stages, hence an accelerated test may cause softening, stiffening or no change in the stress strain curve depending on whether the oxidation factor or the heat factor is predominant or whether the two are in balance. To study after-vulcanization effects the cured stock is, therefore, subjected to an elevated temperature in an inert atmosphere. Ordinarily, it is heated for three to six days in an atmosphere of purified nitrogen at 70° C. The results of such accelerated tests are, in general, in good agreement with natural aging tendencies.

9. *Suitability for air and steam cures.*—Curing in hot air under pressure is relatively slow and promotes oxidation. Hence, speed and antioxidant properties to a large extent govern the ability to give satisfactory air cures. An air oven test is conclusive.

Most accelerators behave the same in open steam as in mold cures. Captax, however, cures faster in open steam.

10. *Stearic Acid Requirements.*—Most accelerators are improved by the use of some stearic acid. Some are harmed by an excess.

Most accelerators require a certain amount of zinc oxide in order to function and this must usually be converted into a rubber-soluble soap for reaction. Thus many accelerators will not cure in extracted rubber—to which no stearic or similar acid has been added—though some of these will do so in the presence of a large excess of zinc oxide.

This whole question is an important one and should be solved for each accelerator by testing it in extracted rubber with and without stearic acid.

The effect of pigments on accelerator cures has already been mentioned. Carbon black absorbs certain accelerators directly, e.g. heptene, vulcanol. Clays also absorb heptene, vulcanol, diphenylguanidine and thiocarbanilide. In at least one case, namely mercaptobenzothiazole, the carbon black affects the cure, apparently due to absorption of the resin acids.

Another effect which must be taken into account is activation of accelerators by other materials and by each other. For example, many materials activate mercaptobenzothiazole, such as lead compounds, bases, amines, etc. Diphenylguanidine and Captax are strongly activating probably by direct reaction.

One of the concerns of the rubber manufacturer, when he buys an accelerator is its stability before use. It has been observed, for example, that a diphenylguanidine masterbatch or complete batch of raw stock, will gradually lose curing strength over several months standing. The xanthates and aldehyde ammonia decompose in a few weeks standing in the air. Paranitrosodimethylaniline exhibits a peculiar tendency to cause a cement batch to become thin. The cause is unknown but it is not due to oxidation.

Thus it is seen that many facts must be known regarding an accelerator's behavior before its suitability for special practical uses may be determined. Many of these facts may be obtained by laboratory tests, such as have been outlined, and uniformity of procedure helps in an accurate classification. However, there are doubtless apt to be eccentricities of individual behavior and special requirements which can only be found by cumulative experience on a production scale.

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Evaluation of Variable-Temperature Cures[1]

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Employing the generally accepted empirical rule that intensity of curing action doubles with a rise of 15° F., relations are developed between the several variables of a cure segment with a constant temperature gradient—viz., "intensity of curing action," "curing effect," time, and temperature—and the constants of such a cure, initial temperature and temperature gradient.

Exact evaluation of cures is extended to schedules involving variable temperatures by the equations showing curing effect as a function of the other properties of a cure. These are the equations of chief practical importance.

Curing effect, the measure of the net value of a schedule in effecting vulcanization, may be determined for a given schedule either by calculation from one of the "effect" equations, by direct reading from one of the several herein displayed graphs of effect *vs.* other properties, or by estimation of the area under an intensity-time curve.

Intensity of curing action measures the importance of a temperature in promoting vulcanization, and the intensity-time curve displays the curing ability of a schedule in its various parts even more accurately than

[1] Presented under the title "The Evaluation of Variable Temperature Cures, with Special Reference to Rubber Footwear and Proofed Goods Schedules" before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

the more usual temperature-time curve.

Examples applying the methods of the paper to typical factory cures are given.

IN VULCANIZING practice "stepped cures," or schedules which comprise a number of periods each subject to either a constant temperature or a uniform temperature gradient, are in general use. Cures of this sort are especially characteristic of the footwear and proofed-goods branches of the industry and are used in the vulcanization of thick objects such as solid tires and rubber rolls. For instance, a "dry heat" or "box cure" for footwear, lasting in all from 2 to 9 hours, may consist of three to six well-defined periods. In a typical case a box cure may have the following parts: a preliminary rise of one or two gradients; a "hold" at a constant temperature adequate to dry out fabric and rubber; a rise of one or two gradients from the drying temperature to the highest temperature of the schedule, during which the intensity of the curing action is increasing; and finally a "hold" at a constant (comparatively high) temperature of such duration as to bring the goods to the proper state of cure.

Where the heater is of large volume with air the medium, it is impossible, even if it were desirable, suddenly to impose upon the stock the maximum curing temperature. Schedules with gradients, while from the practical standpoint both unavoidable and desirable, present theoretical difficulties arising from the lack of a measure of their net curing effects. For example, it is evident that to double the effect of a given constant-temperature cure it is necessary only to double the time, to raise the temperature appropriately, or to increase both the time and the temperature according to easily computable degrees. The inconvenience of a variable temperature within the period is not involved. However, let it be required to alter by a given amount the curing effect of a typical footwear box heat; to reduce the total time of one, retaining, by internal changes in the schedule, the original net effect; to assign relative curing values to several schedules differing as to total time, maximum temperature reached, period at maximum temperature, and period and gradient of approach to maximum temperature; or to do anything else dependent on the evaluation of several entirely different schedules in terms of some unit of curing effect—and no longer is a ready solution available. Consequently, schedules involving variable temperature are generally handled on a purely empirical basis.

The curing effect of a period with a constant temperature may be evaluated as the product of time and intensity of curing action.

Note—The expression "rate of cure" has frequently been used to designate what herein is termed "intensity of curing action" because of the common, perhaps more proper, use of the former term to designate a different quantity than that which we call "intensity"—viz., to designate the rate of change in the properties of a given stock at a given instant. "In-

tensity" is a function of temperature only, something independent of composition of stock or of time, and the writers have therefore distinguished between intensity, I, and rate, R. The distinction between these two quantities and their relation to composition, C, time, t, and temperature, T, are:

$$I = f_1(T)$$
$$R = f_2(I, C, t) = f_2[f_1(T), C, t]$$

"Rate of cure," as defined by this equation, approaches zero as a limiting value for any composition and temperature as the time is increased. This paper is not particularly concerned with rate; its purpose is the analysis of vulcanizing schedules *per se*, independently of composition of stock or other variables which determine "rate of cure."

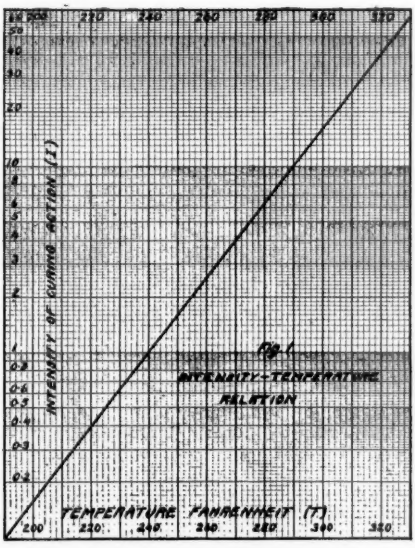
Similarly "curing effect," E, has been employed to designate that quantity depending only on intensity and on time according to the equation

$$E = \int I.dt = \int f_1(T).dt$$

and "effect" has been distinguished from "degree," D, or state of cure as defined by the equation

$$D = \int R.dt = \int f_2(I, C, t).dt = \int f_2[f_1(T), C, t].dt$$

Curing effect pertains to a schedule, degree, or state to a stock; we are concerned here only with the schedule.



As schedules are defined originally in terms of temperatures rather than intensities, a relation between these two quantities is necessary. Various relations have been used, the most generally accepted being those which claim a doubling of the intensity for a given temperature increment. For example, increments ranging from 11° to 18° F. have been claimed as responsible for a doubling of the intensity. With, therefore, the proportionality of effect to time and to intensity and with the dependence of intensity upon temperature according to an empirical exponential relation, it is a very simple matter to evaluate a given constant-temperature

period, or a more elaborate schedule consisting of a succession of such periods.

It is not the purpose of this paper to discuss the validity of any one temperature-intensity relation as against another, but rather to show, on the basis of one such relation, generally accepted and quite well established, how exact evaluation may be extended quickly and conveniently to schedules with variable temperatures. Several years ago, the authors, chiefly with the object of facilitating the consideration of vulcanizing schedules for footwear and proofed goods, developed the equations and convenient graphic methods which will be described herein. The relationships developed are general and apply to any schedule consisting of one or more parts, each characterized by a uniform temperature gradient.

Development of Formulas

The writers have adopted the perhaps most commonly accepted relation between intensity of curing action and temperature—viz., that intensity doubles with a rise of 15° F. Although one of them[2] has found that, in mold cures on a litharge stock, 13° F. produces a doubling of the intensity, in this paper 15° has been used, because (*a*) the experimental work in question was confined to press cures and to a single stock, whereas the formulas herein developed and depending on an intensity-temperature relation had their application largely in dry heats, and also on account of (*b*) the general acceptance of and (*c*) ease of handling the 15° F. rule. Tables based upon this figure have been regularly employed by the industry to facilitate calculations on constant-temperature cures.

In analyzing the effect of a "stepped cure" it must first be divided into parts, each having a uniform rise (or fall) of temperature.

TIME-TEMPERATURE RELATION—Let us consider a period in which there is a constant temperature gradient—i. e., one in which

$$\frac{dT}{dt} = m, \text{ a constant}$$

where t = time in minutes since the beginning of the period
and T = temperature in ° F. at time t

Then the relationship between time and temperature is

$$T = T_0 + mt \qquad (1)$$

where T_0 = temperature at the beginning of the period

TEMPERATURE-INTENSITY AND TIME-INTENSITY RELATIONS—It is convenient to set the intensity at unity for some given temperature and 240° F. has been arbitrarily chosen as the temperature of unit intensity.

Let I equal the intensity of curing action, measured in

[2] Sheppard, "An Experimental Determination of the Temperature Coefficient of Vulcanization with Litharge" presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

such units that $I = 1$ when $T = 240$. Then from the rule that intensity doubles with a rise of 15° F., we have

$$I = 2^{\frac{T-240}{15}} \tag{2}$$

or

$$49.8 \log I = T-240 \tag{2a}$$

whence from (1)

$$I = 2^{\frac{T_0-240+mt}{15}} \tag{3}$$

Simplifying the form by substituting the constants

$$a = 2^{\frac{T_0-240}{15}}$$

and

$$b = 2^{\frac{m}{15}}$$

we have

$$I = ab^t \tag{4}$$

It should be observed that (2) and (2*a*) give intensity in terms of temperature, while (3) gives intensity in terms of time elapsed since the beginning of the period.

TIME-CURING EFFECT RELATION—Let E = curing effect, defined by the equation, holding for a constant value of I,

$$E = It \tag{5}$$

so that $E = 1$, when $t = 1$, and $I = 1$ (or when $T = 240$)

Under a temperature gradient, i. e., when I varies with t

$$dE = I.dt$$

and

$$E = \int_0^t I.dt$$

From (4)

$$E = \int_0^t ab^t.dt$$

or

$$E = \frac{a(b^t-1)}{\ln b} = \frac{a(b^t-1)}{0.04621\, m} \tag{6}$$

CURING EFFECT–INTENSITY AND CURING EFFECT–TEMPERATURE RELATIONS—From (4) and (6) we get

$$E = \frac{I-a}{0.04621\, m} \tag{7}$$

or

$$I = 0.04621\, mE + a \tag{8}$$

From (2) and (8) we get

$$0.04621\, mE + a = 2^{\frac{T-240}{15}} \tag{9}$$

SUMMARY OF RELATIONS—By means of these equations, when for any curing period with a constant rate of temperature change there are given the constants T_0 (initial temperature) and $m(=dT/dt)$ and any one of the four variables t, T, I, and E, the other three variables may be calculated.

For convenience, the equations developed, together with obvious expansions of equations (6), (8), and (9), are summarized as shown in the accompanying table.

Application to Cure Schedule Evaluation

INTENSITY OF CURING ACTION—Intensity of curing action at any given temperature may be obtained from equation (2) or (2*a*); or, as a function of time, from (3). These two relations yield straight lines when graphed on semilogarithmic paper. Figure 1, in which equation (2) has been so plotted, enables intensity to be read instantly for any given temper-

ature with an accuracy of about 1 per cent, an accuracy exceeding the nicety with which equation (2) conforms to the facts.

Variables Related	Equation Using Primary Constants	Equation Using Secondary Constants
T,t	$T = T_0 + mt$	
I,T	$I = 2^{\frac{T-240}{15}}$	
	$\log I = \frac{T-240}{50}$ (approx.)	
I,t	$I = 2^{\frac{T_0-240+mt}{15}}$	$I = abt$
E,t	$E = \frac{2^{\frac{T_0-240}{15}}(2^{\frac{mt}{15}}-1)}{0.04621\ m}$	$E = \frac{a(bt-1)}{0.04621\ m}$
I,E	$I = 0.04621\ mE + 2^{\frac{T_0-240}{15}}$	$I = 0.04621\ mE + a$
E,T	$0.04621\ mE + 2^{\frac{T_0-240}{15}} = 2^{\frac{T-240}{15}}$	$0.04621\ mE + a = 2^{\frac{T-240}{15}}$
	$3025\ mE + 2^{\frac{T_0}{15}} = 2^{\frac{T}{15}}$	

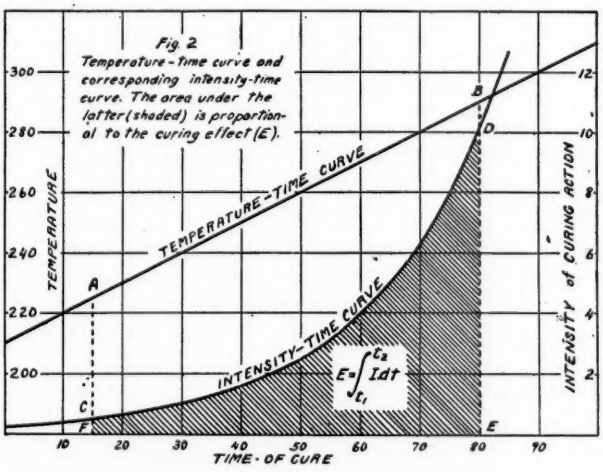
Intensity is a quantity of importance per se in that it is the function which must be known whenever it is desired to transform, without change in curing effect, a constant-temperature cure from a given to a new time and temperature. Such transformations are made according to equation (5), and in general any problems on constant-temperature cures involving the three variables of time, temperature, and curing effect are handled by equation (5) after the intensity equivalent of temperature has been obtained through, say, equation (2*a*) or Figure 1. Intensity is important also as a prerequisite both to the development of the expressions for the evaluation of variable temperature schedules and to a very useful graphic presentation of a curing schedule, as shown below.

Curing Effect—The first step in the determination of the curing effect of any given schedule is to divide the entire schedule into periods of uniform temperature gradient so that each becomes subject to the equations developed herein. Then a single period can in practice be evaluated in any one of several ways: (1) by direct use of one of the equations involving effect, E, as a variable, (2) by estimating the area under an intensity-time curve, or (3) by reading from a graph based upon one of the "effect" equations.

(1) *Computation from Equation*—Equation (6), (7), or (9), or the expanded form of one of these, as shown in the summarizing table of equations, may be used for direct calculation of curing effect. Of these the expanded form of equation (6) is ordinarily the most useful as in it E is given in terms of

quantities usually known without calculation—namely, initial temperature, time, and temperature gradient. Generally speaking, direct use of one of these equations is not the most convenient way of determining the curing effect; as a rule, either procedure (2) or (3) is more convenient.

(2) *Estimation of Area*—Figure 2 illustrates how the intensity-time curve may be used to determine curing effect. The straight-line segment AB represents the temperature-time relation of a cure period in which there is a uniform temperature gradient, here equal to 10° F. in 10 minutes (or $m = 1$). In this case initial temperature, T_0, is 225° F.,



and time, t, after the attainment of T_0, is 65 minutes. The exponential curve CD is the corresponding intensity-time curve, and in view of the fundamental equation for curing effect,

$$E = \int_{t_1}^{t_2} \mathrm{I}.dt$$

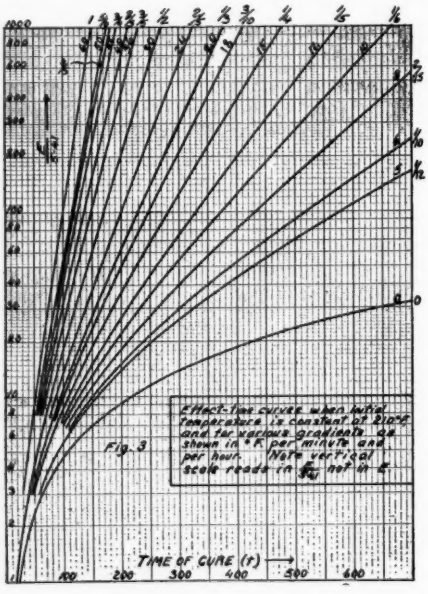
the area between CD and the time coördinate, or $CDEF$, is proportional to effect. CD may be quickly drawn as a smooth curve through five or six points plotted from such almost self-evident values of intensity as $I = 1/2$ for $T = 225$, 1 for $T = 240$, and 2 for $T = 255$, and so forth, or by plotting any other values for intensity, as derivable at a glance from the intensity-temperature graph of Figure 1.

The estimation of the area $CDEF$ may be made in any of the well-known ways as, for example, by (*a*) use of the planimeter, (*b*) counting of squares, (*c*) weighing a piece of paper cut to the figure the area of which is to be estimated.[3] The accuracy of any of these methods depends on the precision both with which the curve is drawn and with which its area is

[3] Fol, *India Rubber J.*, **45**, 679 (1913).

estimated, but the resultant accuracy greatly exceeds that of the basic empirical relation. For example, E for the case illustrated in Figure 2 when calculated from equation (6), equals 209; whereas when determined by counting squares under CD as actually drawn, for purposes of illustration rather than computation, we obtain $E = 207$.

On two standard grades of graph paper deviations of 0.5 and 2.5 per cent, respectively, have been found in the weight of equal areas cut from different parts of the same sheet. The uniformity of graph paper is therefore seen to be somewhat variable and the paper-weighing method should be used only on paper that has been found to be uniform, and even then it is



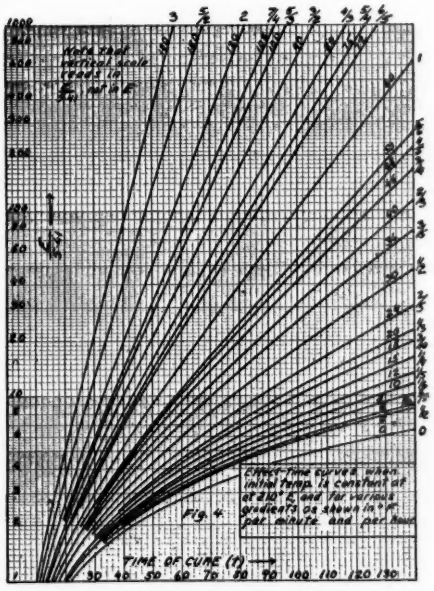
good practice to compare the weight of the cut-out for estimation with that of a rectangle of known area cut from the same piece of paper.

No attempt has been made in this paper to derive equations for E where the temperature gradient is non-uniform. There are several reasons for this. Firstly, the great majority of variable temperature schedules, in strict conformity with the instructions for executing them, call for a series of uniform gradient periods and therefore fall within the scope of the relations here developed. Secondly, the integration to obtain E for non-uniform gradients is more complicated and leads to cumbersome final equations, and is, moreover, unnecessary because the graphic method of estimating E of Figure 2 is applicable just as readily to variable as to constant temperature gradients. For a cure with a variable gradient, the procedure is to plot an intensity-time curve, based on the

temperature-time relation (whether that be fixed by definition or empirically determined) and to estimate the area under this curve exactly as in the case of a uniform gradient.

The intensity-time curve, when drawn to an equal-division scale, gives one the proper picture of the relative importance of the low and high temperatures of a schedule, something which the temperature-time graph does not do. This, of course, is because intensity is the quantity which measures the importance of a given temperature in promoting vulcanization.

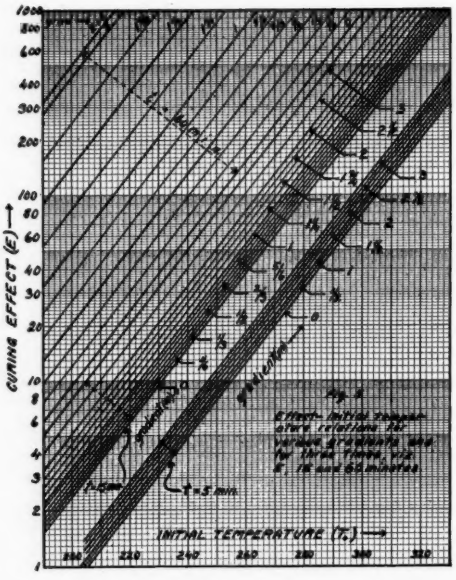
(3) *Direct Reading from Graph.* Considerable attention has been given to the development of graphs designed to



show curing effect as a function of the other properties of a schedule, so that E might be read off directly without recourse in an individual case either to computation from an equation, as in (1), or to graphing the cure in terms of intensities with subsequent estimation of an area, as in (2). It has not, however, seemed possible to devise any single graph which will enable effect to be read when the other properties which define the cure are given. The difficulty lies in the number of these other defining properties. The problem of graphically presenting effect may be stated as that of drawing a locus for the equation connecting the dependent variable E with the three independent variables which are necessary to define a cure segment. For example, in the expanded form of equation (6), which is the most convenient one either for computation in a specific case or as the basis of a graph, the variables

on which effect E depends and which define the cure are initial temperature, T_0, gradient, m, and time, t. The equation is therefore four-dimensional and incapable of graphic representation. This is true also of equations (7) and (9).

While, therefore, the writers have been unable to accomplish the theoretical objective of displaying a graph which at one reading and without any calculation would enable E to be read for any values of the other three variables, they have, however, designed several graphs which individually partially meet the objective, and which as a group accomplish in nine out of ten cases the practical purpose of enabling quick determination of E to be made. These several graphs designed for the ready derivation of E, their construction, use, and limitations, will now be described.



(a) Effect-time curves with gradient as variable parameter and with initial temperature fixed at 210 degrees. Figures 3 and 4, which differ only in their time scales, display families of curves, each of which plots the quantity $E/5.41$ against t, the individual curves being subject to different values of m, and all curves being subject to the condition $T_0 = 210°$ F. The values of m, ranging from 0 to 1 in Figure 3 and from 0 to 3 in Figure 4, and so chosen as to cover the gradients in most general use, are marked on the individual curves as fractions and in degrees per hour.

When in the expanded form of equation (6) the substitution $T_0 = 210$ is made, we get

$$\frac{mE}{5.41} + 1 = 2^{\frac{mt}{15}} \qquad (10)$$

By substituting in equation (10) successively the values of m, we get the equations which govern, and which have been used in

computing, the values of $E/5.41$ and of t for the individual curves.

When it is desired to obtain the curing effect for an initial temperature of 210° F., the procedure is, on the curve for the given gradient, to read off for the time in question the value of $E/5.41$ and to multiply this by 5.41.

When, as usual, the initial temperature is higher than 210° F., the procedure is this: The value of $E/5.41$ is read off for the specified gradient and for an initial temperature of 210° F., but for the time required to bring the temperature at the gradient in question from 210° F. to the final temperature obtained by applying the specified gradient to the specified initial temperature. Also the value of $E/5.41$ is read off for the specified gradient, for an initial temperature of 210° F., and for the time required to raise the temperature from 210° F. to the specified initial temperature. The difference between the former value of $E/5.41$ and the latter multiplied by 5.41 yields the effect for the specified initial temperature.

This working rule for deriving effect from Figure 3 or 4 in cases where the initial temperature is above that assumed in the construction of the graphs is, of course, based upon the fact that the effect is cumulative with time, that the total effect of a period is the sum of the separate effects for any parts into which the period may be divided. We may express the rule concisely by:

$$E_{T_0>210} = \int_{T_0}^{T} Idt = \int_{210}^{T} Idt - \int_{210}^{T_0} Idt \qquad (11)$$

where T_0 = given initial temperature

T = the final temperature which follows from the values of T_0, m, and t given

As an example of deriving E from Figure 4, let us take as a typical case the following numerical values:

$T_0 = 240$, $m = 1/3$, and $t = 90$

From equation (1)

$$T = 240 + \frac{90}{3} = 270$$

Time to reach 270° from 210° F. = 180 minutes
Time to reach 240° from 210° F. = 90 minutes

Then reading from Figure 4,

$\frac{E}{5.41}$ for the range 210° to 270° F.—i. e., for 180 minutes = 44.8

and

$\frac{E}{5.41}$ for the range 210° to 240° F.—i. e., for 90 minutes = 9.0

$\therefore$ E for the specified conditions = $(44.8-9.0) \times 5.41 = 194$

On account of its more open time scale, and therefore greater accuracy, Figure 4 is preferred to Figure 3 for cases within its scope. There are two reasons for adopting $E/5.41$ instead of E as the unit in the ordinate of these two sets of curves: (*a*) The ordinate of the graph form conveniently accommodates only 1000 units and, while 1000 is an unusually high value of E for cures used in practice, it is not nearly high enough, in cases where m is small and T_0 high, for one of the hypothetical cures—namely, the one stretching from 210° F. to the actual final temperature, which it is necessary, according to its mode of usage, to evaluate from the graph as a prerequisite to obtaining E for the given cure. Therefore, it is desirable to make the unit space on the graph stand for a multiple of a unit of E. (*b*) The multiple chosen is 5.41, since it is convenient to use that number (equation 10), and 5.41 increases the range of the graph in respect to E to a fairly satisfactory degree.

The disadvantages of Figures 3 and 4 as means of quick derivation of effect are: (*a*) the necessity of making two readings

Table I—Summary of Procedures for Determining Curing Effect

Procedure	Figure	Description of Graph	Process in Brief	Advantages	Disadvantages
(1)	..	.....	Compute E from an equation—e. g., equation (6)	Most accurate method, and one on which all others depend	Usually most laborious method
(2)	2	$T-t$ and $I-t$ curves Typical case only	Estimate E from area under an $I-t$ curve, as determined in one of following ways:	(1) An intensity graph is obtained which is per se useful, as affording a truer picture of curing tendencies than a temperature graph (2) Always applicable, even to conditions outside range of Figures 3, 4, 5, 6, and 7 and to cases of variable gradient, not covered by equations	Conversion of temperatures into intensities, graphing of latter, and estimation of area under curve, usually require more time than reading E from graph as in method (3)
(*a*)			By planimeter	Probably quickest way to estimate area	
(*b*)			By counting squares		
(*c*)			By weighing paper cut-out		Applicable only to graph paper of ascertained uniformity of weight
(3)			Read E directly from one of graphs involving E as variable, as given below:	Quickest way to obtain E for all cases within limitations of graphs, as involving no graphing and none or a minimum of calculation	Limited to cases within range of one or other graph
(*a*)	3 4	$E-t$ curves, with m as variable parameter and T_0 constant at 210	For given gradient read $E/5.41$ for time necessary to raise T from 210 to (1) given final temperature, (2) given initial temperature. Subtract (2) from (1) and multiply by 5.41	Handles any time period within range of Figures 3 and 4, and without necessity of breaking it up into arbitrary parts with reading of E for separate parts	(1) Limited to individual gradients and time range used in Figures 3 and 4 (2) Necessary usually to make two readings (3) Necessary to multiply reading by 5.41 (4) Less accurate than (*b*) or (*c*), because of necessarily more condensed E scale
(*b*)	5	$E-T_0$ curves, with m as variable parameter and with t fixed at three values—60, 15, and 5	Divide cure into periods of 60, 15, and 5 minutes, and for each read E for given gradient, and for value of t and T_0 pertaining to period. Sum of these several values of E is E for given period	(1) Applicable to any initial temperature within range of graph (2) More accurate than (*a*), for reason stated under (*a*) (3) Reads directly in E; no multiplication necessary	(1) Limited to individual gradients shown in figure (2) Limited to periods which are multiples of 5 minutes (3) Necessary usually to subdivide period and make separate readings for the several parts
(*c*)	6 7	$E-m$ curves, with T_0 as variable parameter and with t fixed at three values—60, 15, and 5	Proceed exactly as in (*b*) above	(1) Applicable to any gradient and initial temperature within range of the graphs. Equal spacing of curves makes interpolation for unmarked values of T_0 easy (2) More accurate than (*a*) for reason stated under (*a*) (3) Reads directly in E; no multiplication necessary	(1) Limited to periods which are multiples of 5 min. (2) Necessary usually to subdivide period and make separate readings for several parts

with some prior (though simple) calculations; (*b*) the effect can be read only for those gradients shown on the graphs; (*c*) notwithstanding the use (in both figures) of $E/5.41$ as unit for the ordinate and an unusually great time range (in one of the figures), cures with quite low gradients and high initial temperatures will be found outside the range of either figure. Within their ranges, however, Figures 3 and 4 are usable for all gradients marked on them and these are the more common ones.

(*b*) *Effect-initial temperature curves with gradient as variable parameter and with time fixed at 60, 15, and 5 minutes, respectively, for each of three families of curves.* In Figure 5, E is plotted against T_0, each line being subject to the value of m with which it is marked and to the value of t with which the entire family of curves to which it belongs is marked. There are three families in the one graph subject, respectively, to the following values of t—60, 15, and 5 minutes. The values of the parameter m range from 0 to 3 except in the family where $t = 60$ minutes, wherein m ranges from 0 to 2. In the family subject to $t = 5$ it has been possible, on account of the proximity of lines to each other, to use only a limited number of values of m; for $t = 15$ and for $t = 60$ more numerous values of m are capable of display.

The curves in each family of Figure 5 have been computed by substituting in the expanded form of equation (6) a value for t. When this value is $t = 15$, we get from equation (6)

$$E = \frac{21.64\ (2^m - 1)}{m} \times 2^{\frac{T_0 - 240}{15}} \qquad (12)$$

The equation for an individual line is then obtained by substituting a value for m in equation (12). As the resulting equation is exponential in E and T_0, the plot is a straight line on the semi-logarithmic graph paper. The other two families are based on equations analogous to (12), obtained by substituting 60 and 5, respectively, for t in equation (6).

Figure 5 yields at once a reading for the effect of any cure within its range and subject to a gradient shown and to a time of 5, 15, or 60 minutes. When the time is otherwise than one of these three periods but is a multiple of 5 minutes, the procedure is to break the period up into sections such that each involves one of these three displayed times. As an example we may take the numerical values used in illustrating procedure (*a*),

$T_0 = 240,\ m = {}^1/_3,\ t = 90$

E for 60 minutes, going from 240° to 260° F. = 100
E for 15 minutes, going from 260° to 265° F. = 41.8
E for 15 minutes, going from 265° to 270° F. = 51.4

$\therefore E$ for 80 minutes going from 240° to 280° F. = 193

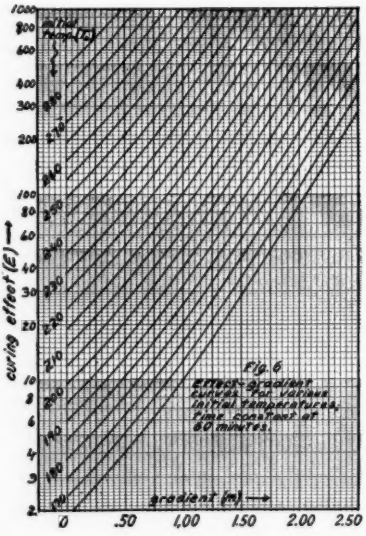
Compared with Figures 3 and 4, the advantages of Figure 5 are: (*a*) it has greater accuracy due to its more open E scale; (*b*) cases as a rule can be determined by it somewhat more quickly than by Figure 3 or 4. The disadvantages of Figure 5 are: (*a*) the limited number of gradients displayed, particularly for the 5-minute cure; (*b*) cures to be handled must have time periods which are multiples of 5 minutes. Figure 5 is preferred to 3 or 4 for cases within its range.

(*c*) *Effect-gradient curves with initial temperatures as variable parameter and with time fixed at 60, 15, and 5 minutes, respectively, for each of three families of curves.* In Figure 6 there is plotted E against m, T_0 being shown as a variable parameter, and t being constant at 60 minutes. Figure 7 employs the same variables and variable parameter, but in this two families of curves are shown characterized, respectively, by $t = 15$ and $t = 5$. These figures have been graphed from the same data employed in graphing Figure 5—namely, data derived from equation (12). The essential difference between Figures 6 and 7 and Figure

5 lies in what have been chosen as independent variable and as variable parameter.

These figures are used very similarly to Figure 5, by dividing the cure into parts of 60, 15, and 5 minutes' duration and finding E for the whole as the sum of the values of E for the parts.

Compared with Figure 5, Figures 6 and 7 have the advantage of covering all gradients within their range, but the disadvantage of having initial temperature displayed at only fixed intervals as a parameter. This disadvantage, however, will not be found so objectionable as the parametric treatment of gradient in Figure 5 or Figures 3 and 4. It will be found almost as easy in Figures 6 and 7 to estimate the position of a curve corresponding with an initial temperature not shown on the graph as to estimate intermediate values on the gradient or effect scales. Generally speaking, procedure (*c*) is more convenient than procedure (*a*) or (*b*) and is preferred when applicable. Procedure (*c*), like (*b*), is limited to cases where the duration is a multiple of 5 minutes.



Summary of Procedures for Determining Curing Effect—In the belief that a table of the several procedures for determining curing effect, summarizing the advantages and limitations of each, will aid in the choice of the best method for a given case, Table I has been drawn up. In general the writers' preference is to display a cure through both temperature-time and intensity-time graphs similar to Figure 2, but to evaluate it by reading the curing effects (E) of its several uniform gradient segments directly from one of the "effect" graphs.

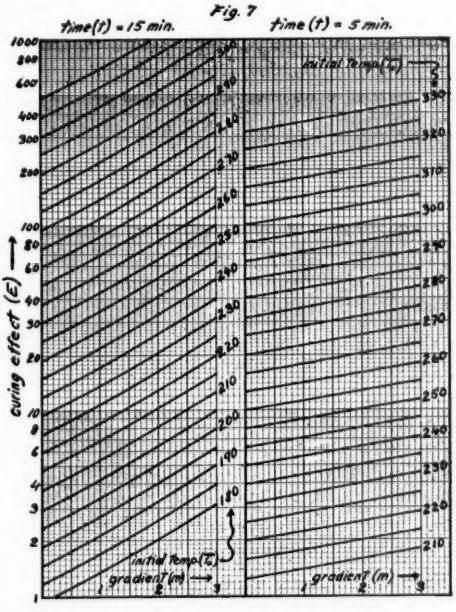
Illustrations from Plant Practice

Figures 8 to 11 show some typical curing schedules illustrating a variety both of product and of type of cure, and graphed to display intensities as well as temperatures. The

intensity-time curves are the lowest ones, the areas subtended by which are shaded and (as between the several schedules in each figure) are proportional to the curing effects. The curing effects have been tabulated on each graph for the cures displayed thereon.

Figure 8 shows three footwear box cures, of quite diverse curing effects, the "heavy" cure being about 66 per cent more severe than the lightest or "surf" (bathing shoe). The restrained curing activity of the "heavy" heat during its preliminary "warming up" and "drying out" periods, *ABFK*, is well reflected in the corresponding low-lying intensity curve and in the attainment of a curing effect, up to the point *K* at the end of the "drying out" period, of only 34 out of a total of 391 for the whole schedule. Contrasted with this in

Fig. 7



an unmistakable manner by the mode of display used is the quick attainment of a curing condition in the "surf" cure. The temperature curves for these two schedules fail to convey, except by inference, the important fact that at its highest temperature the "heavy" heat is promoting vulcanization twice as actively as the "surf" at its peak. This fact is, however, expressed directly by the intensity curves through their relative heights. It is for reasons of which this is but a particular case that the writers believe the plotting of intensities greatly to promote the clear conception of vulcanizer schedules where variable temperatures are employed.

The curing effects shown in the upper left corner of Figure 8, and also on Figures 9 to 11, were obtained by direct reading from one or other of the "effect" graphs—Figures 3 to 7.

Extreme accuracy is neither to be expected nor, in view of the only approximate character of the basic relation, necessary. An agreement within about 1 per cent, as among evaluations read from different "effect" graphs or as between such

Table II—Values of E for Various Parts of Heavy Footwear Box Cure as Derived by Several Procedures

Period	T_0	t	m	E Obtained by Procedure			
				(1) Calcd.	(3) (*a*) Read from Figures 3 and 4	(3) (*b*) Read from Figure 5	(3) (*c*) Read from Figures 6 and 7
AB	160	60	1/3	..	..	..	2.1
BF	180	180	1/6	..	..	.. . 7.7 12.0	4.7 7.7 12.2 24.6
FK	210	30	0	7.5	7.6	3.75 3.75 7.5	3.75 3.75 7.5
KL	210	60	1/6	..	19.2	19.2	19.4
LM	220	180	1/4	..	244.5	..	35.3 69.5 138.5 243.3
MN	265	30	0	95.3	..	46.8 46.8 93.6	47.0 47.0 94.0

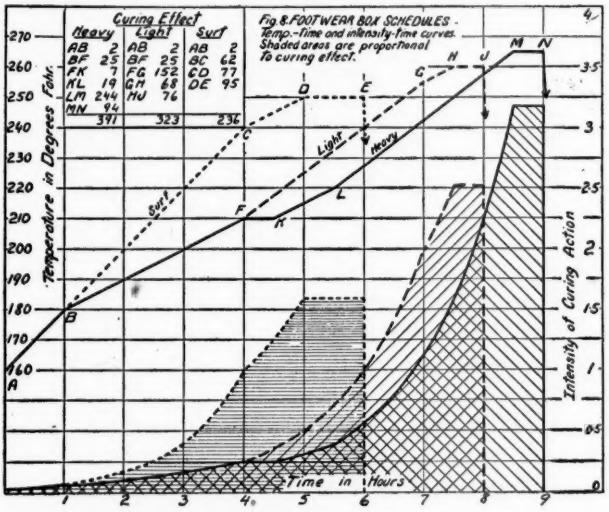
an evaluation and the "correct" value got by calculation, may be expected. Table II brings out this point. It details the values of E obtained by various procedures for the several segments of the "heavy" cure in Figure 8. Agreements of the same order were obtained in evaluating the effects for the other schedules illustrated.

In Figure 9 two dry-heat cures, with air pressure, for footwear are shown. Although there is a considerable divergence between the two schedules, they are in general of the same order of curing effect as the box heats of Figure 8. That such is the case, notwithstanding their much shorter durations, is of course due to the higher intensities employed in the pressure cures and also to the much more abrupt "rise."

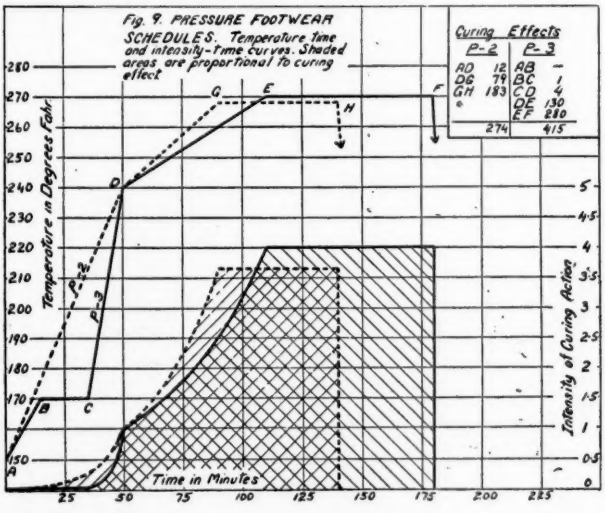
Schedules for dry-heat cures on proofed goods of single and double texture are given in Figure 10. That single textures are given a dryer or more complete cure than double textures is a matter of common knowledge, but that the single cure has three times the severity of the double is hardly obvious even from an inspection of the temperature schedules. The curing effects bring out this more exact relation in the severities, however, and the intensity graphs with their subtended areas create an impression of the same outstanding difference in the two cures.

Figure 11 shows cures for $3^1/_2$- and 8-inch solid tires. These schedules, although "stepped," do not involve variable tem-

peratures in the sense of a variation within a given step or segment of the cure. They can, therefore, contrary to the cases illustrated in Figures 8, 9, and 10, be evaluated without recourse to one of the equations developed herein for variable-

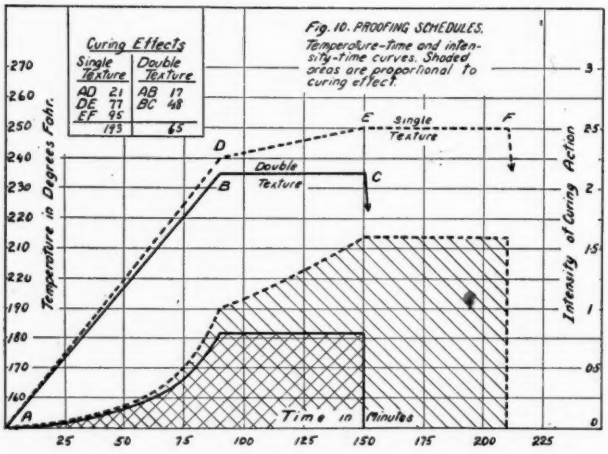


temperature cures or to any graphic method depending upon these equations, simply by taking the curing effect of each segment as the product of its time and intensity (equation 5). Nevertheless it is useful here, as in the other cases, to plot

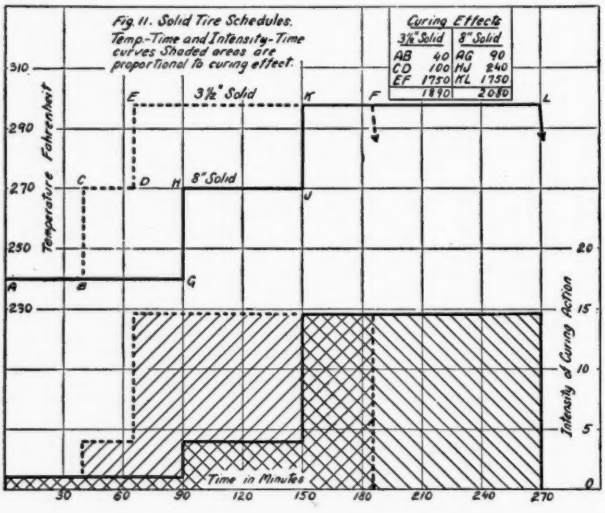


an intensity-time graph. It will be noted from Figure 11 that, although the schedules for the two tires are quite different in their total times, their curing effects are only moder-

ately different. This, of course, is consequent upon that segment responsible for most of the curing, the one at 298° F., being of equal duration for both cases (120 minutes), the



diversity of time being in the early, low-intensity portions, comparatively unimportant from the standpoint of vulcanization (but of course essential to heat penetration).



Acknowledgment

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Dispersion of Pigments in Rubber[1]

I—Microscopical Studies of Agglomeration and Flocculation

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A literature review has been given dealing chiefly with the different factors that influence and regulate the dispersion of pigments in rubber, especially agglomeration and flocculation.

Suggestions have been offered in regard to the validity of different physicochemical dispersion laws for the system rubber–pigment.

The nature of agglomeration and flocculation of carbon black and zinc oxide has been described.

Experimental evidence has been presented showing changes taking place in the dispersion of pigments during vulcanization.

The distribution of carbon-black pigments in highly compounded treads has been discussed. The particles appear to assume a loose network formation which perhaps is an indication of the reënforcement of the system.

IN A stimulating paper Wiegand[1,*] outlined several interesting compounding problems on pigment dispersion in rubber (in the following the word "pigment" will be used in its rubber technological sense). He emphasized the role of the electrical charge upon the pigment particles, the value of softeners, the order of mixing, and the viscosity of

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

* Numbers in text refer to bibliography at end of paper.

the rubber in obtaining an optimum dispersive effect. The reënforcing capacity of pigments was understood as due to increase in surface energy of the system. When a true reënforcing pigment is added to rubber, there is an improvement of the quality up to an optimum and then, if the addition is continued, a decline to the original properties or even below. Two different tendencies prevail; up to the optimum, reënforcement is predominant; beyond the optimum the rubber simply becomes diluted. Incomplete wetting and agglomeration of the particles impedes the rate of addition of surface energy to the system. He pointed out the importance of retarding the agglomeration of pigment particles. These particular parts in Wiegand's paper have been referred to because they define the viewpoint from which the subject of dispersion has been approached in the following investigations.

In this paper the tendency of particles to pack and form secondary units during milling has been defined as "agglomeration," whereas any more or less dense formations taking place from completely dispersed particles during vulcanization has been defined as "flocculation." The word "aggregation" has been used in cases where it has not been possible to draw a line between agglomeration and flocculation.

Theoretical Part

Several investigators have shown that agglomeration of the filler particles affects the tensile properties of the system rubber-pigment to a considerable extent. Schippel[2] and later Green,[3] studying the volume increase of compounded rubber under strain, found that the rubber when stretched tended to separate from the surface of larger particles and formed vacuoles. According to Green, the agglomerates can be either soft and break up when strain is applied to the rubber, or hard and act as individual particles. In the case of carbon black, they evidently produce the same effect as grit and are partly responsible for the grain in calendered treads and for the heating effect during the service of a tire.

Flocculation of pigments in rubber has been described by Depew and Ruby,[4] who assert that, among other things, it accounts for the heating up of tire treads heavily compounded with carbon black. Green[5] pointed out that flocculation probably takes place when the mobility of the rubber is at its highest—i. e., during vulcanization—and he attributes to it part of the toughening effect of carbon black in vulcanized rubber. Discussing this process, Greider[6] stated that flocculation of pigments need not imply that the surfaces of the particles are not in complete contact with the rubber matrix at every point, but only that the particles have drawn together in groups or clumps. These processes have further been studied by Hardman[7] who demonstrated the agglomeration of antimony pigments. Martin and Davey[8] and also Green[9] have described the flocculation of zinc oxide and

the deflocculating effect of fatty acids. Pohle[10] has shown that measurements of light absorption of compounded rubber give important information about the degree of the mixing process and the tendency of the particles to pack and form secondary formations. The main factor in regulating the degree of agglomeration and flocculation of the pigments seems to be the wetting of the particles by the rubber. Green[5] states that the more effective the wetting the more complete is the dispersion and the less tendency there is to agglomeration during the mixing of the compound. A high surface attraction between rubber and pigment tends to check flocculation. Zinc oxide is wetted well by rubber and disperses satisfactorily in large quantities, whereas carbon black is wetted less readily, which probably accounts for its tendency to flocculate during vulcanization. He has also shown[3] that coarse fillers, classified as inerts, such as whiting, aluminum flake, and asbestine, which have very little reënforcing effect, are not readily wetted by the rubber. They show a tendency to carry air into the stock, and gaseous films, surrounding the particles, are present in the compound. Endres[11] asserts that a filler cannot be completely dispersed on the mill unless the rubber wets it. The degree of wetting determines the effective particle size of the filler and also the attachment between the particle and the rubber. Chemically active and inactive pigments differ considerably in regard to wetting properties during vulcanization. The investigations of Martin and Davey[8] and Bedford and Winkelmann[12] indicate that chemically active pigments, which act as inorganic accelerators, are dissolved in the rubber during vulcanization, forming metallic soaps with organic acids present in the system. These soaps probably are responsible for improvement in dispersion. The adsorptive power of the particle has further been studied by Thies[13] and by Twiss and Murphy.[14]

The surface energy, and consequently agglomeration and flocculation, are further regulated by the particle size of the pigments. Wiegand[15] and more recently Dawson[16] have established the relation between particle size and reënforcing effect for several pigments. It has further been studied by Greider,[17] and by Spear,[18] and the latter has advanced the theory that the reënforcing effect–particle size curve must go through a maximum.

Spear and Moore[19] demonstrated, in regard to carbon black, the possibility that the effect on tensile strength and stiffness is produced independently by separate fractions of the pigment differing in particle size.

Microscopical methods for determination of particle size have been developed and studied by Green,[20] Perrott and Kinney,[21] Peterfi,[22] and Pohle.[23] Ever's[24] measurements of particle size of fillers by sedimentation and Stammberger's[25] work on filler dispersion in rubber as determined by diffusion methods are also of interest. The size of the filler particles in rubber compounding has further been considered by

North,[26] Twiss,[27] Pickles,[28] Endres,[11] and Hock and Bostroem.[29]

The particle shape has been studied and discussed by Vogt and Evans[30] and by Schidrowitz.[31] The nature of the surface structure of the pigment has been considered by Katz and Bing,[32] and North.[33] The uniformity of the particles by Green,[20] Ingalls,[34] and Greider,[6] and the plasticity of rubber, by Burbridge,[35] Burlston,[36] and Griffith.[37] Burbridge[38] and Kroeger[39] discuss the aging of rubber and dispersion of pigments.

There are still other physical properties which may influence the behavior of the pigment when incorporated in rubber. The thermal properties are considered in papers by Williams[40] and by Bierer and Davis,[41] and the electrical properties are reported by the Bureau of Standards.[42] The relation between acidity of rubber and dispersion has been studied by Whitby.[43] Finally a paper by Hauge and Willaman[44] regarding the effect of hydrogen-ion concentration of the medium on the adsorption of different carbons is of interest.

There is, however, but little information in regard to the magnitude of the interfacial force, which keeps the pigments dispersed—i. e., the surface energy or the tension of the rubber-pigment interface. Thus far the only method of making a practical evaluation of this force has been to determine the formation of vacua or volume increase of a rubber-pigment mix under strain as has been shown by Green.[3] During recent years, there has been a tendency to explain dispersive processes in the system rubber–pigment according to physicochemical or thermodynamical laws. Bedford and Winkelmann's[12] observations in regard to the solution of chemically active pigments during vulcanization can be explained according to Harkins'[45] theory of emulsification. Hock[46] has developed a calorimetric method for determination of the total boundary surface energy between rubber and fillers and has further applied the Helmholtz-Gibbs equation to the filler problem. His results indicate that the bond between zinc oxide and rubber is considerably greater than that between rubber and carbon black. However, these investigations cannot be considered final.

Confirmation of the extent to which various physicochemical dispersion laws, established for other systems, are valid for the system rubber–pigment is of great theoretical importance. Pickles[47] emphasizes the importance of the proximity of the reactants in reactions in solid or viscous media, and Martin and Davey[8] assert that flocculation of zinc oxide seems to depend on the distance between the particles not exceeding a certain limiting value. These observations seem to give cause for investigation whether von Smoluchowsky's[48] mathematical coagulation theory can be applied to the flocculation which takes place during vulcanization of rubber. On the other hand, Galecki[49] and

Oden[50] have shown that a sol containing particles of different sizes is less stable than one composed of particles of the same size. This fact evidently conforms with observations of Ingalls[34] in regard to uniformity of pigments. According to H. D. Murray[51] a few large particles in a highly dispersed system, in case of flocculation, will act as nuclei for the others. Klein[52] asserts that non-electrolytes are capable of coagulating colloids, the dispersed particles absorbing capillary substances on their surfaces. Such non-electrolytes and, in addition, electrolytes present in the rubber and different products formed during vulcanization from sulfur or other ingredients may be adsorbed on the surface of the dispersed particles, causing changes in the dispersion of the pigments. Pohle[53] has shown that certain fillers act chemically, presenting changes in the adsorption colors on their surfaces during vulcanization and also bringing about definite changes in the permanent dispersion.

According to Sulman[54] the force of flocculation resides in the interface between the solid and the liquid phase and the flocculation is due to the incompleteness of wetting of pigments by the continuous phase. Selective wetting effects always occur in the direction of the greatest possible reduction of interfacial energy and for complete wetting interfacial tension is nil, a condition which coincides with complete deflocculation. This conception can be developed further if we assume that rubber is a homogenous dispersing agent towards the pigments, the latter are uniform and of colloidal dimensions and possess electrical charges and there exists a potential difference between the surface boundary and the surrounding rubber.

Dispersion and flocculation can in such a case be explained by changes in the distribution of surface energies. A mathematical expression for these changes has been developed by Green and Halvorsen.[55] They can also be applied for the system rubber–pigment, if the above assumptions are considered. These theoretical aspects will, however, be discussed more thoroughly in a future paper.

Experimental

Microscopical methods were used in the experimental work for following the dispersion of the pigments in rubber and the nature of agglomeration and flocculation. Each reënforcing pigment was first studied in combination with rubber alone and then later more and more complicated systems were built up, the dispersive changes being followed in the various instances. The rubber and pigments were standardized in regard to chemical and physical properties and the various compounds prepared under the same milling conditions. Uncured compounds were studied microscopically

Note—In general, this consisted of breaking down 400 grams of rubber for 4 minutes on 12-inch (30-cm.) laboratory mills, adding the pigments and sulfur as quickly as possible, and then sheeting off to 100 gage. The total time on the mills varied from 8 to 13 minutes depending on the type of stock.

in regard to dispersion and agglomeration of pigments using a "Quetschkammer," described by Dannenberg[56] (which consists of a small chamber in which the compound can be squeezed between glass rendering it transparent for microscopical examination), either in transmitted light or with dark-field illumination. Compounds cured under standard conditions were studied in sections prepared according to a modification of the method of Green,[57] the general principle being to harden the sample with sulfur chloride and to cut suitable sections with a microtome.

RUBBER AND CARBON BLACK—Five-tenths and 1 per cent mixes of carbon black in rubber were most suitable for microscopical studies of this pigment. It was found that the particles during milling preferentially tend to aggregate around any larger nucleus present in the rubber—i. e., resin or foreign matter. It was not possible to determine the particle size of the black. According to Barnard (communi-

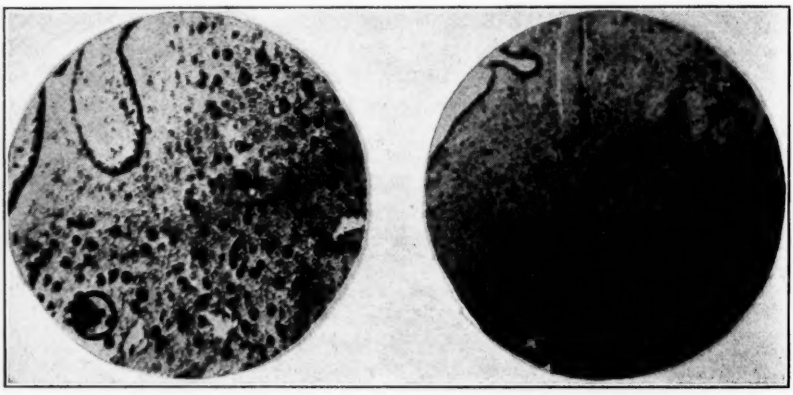

Figure 1—30 minutes at 140° C. Figure 2—60 minutes at 140° C.
Rubber-Carbon Black-Sulfur. 690 ×

cated by Wiegand) it ranges from 40 to 50 millimicrons, as measured with ultra-filters. Microscopical determination of particle size in dark field by counting of the particles when weight and volume of rubber and pigment are known does not give satisfactory results, as the rubber itself contains a large number of ultra-microns originated by dust, etc., for which it is difficult to obtain a correction factor. It was, however, possible to discriminate between seven different types of black from the degree of blackness of a compound containing 0.5 per cent of pigment.

RUBBER AND ZINC OXIDE—The average particle size of the pigment was determined as 0.49 micron in a 1 per cent mixture in rubber. It is probably somewhat smaller than this, since a small portion of the pigment is not resolvable under the microscope. The dispersion was homogenous, agglom-

erates were not noticed, and the particles seemed to possess their original shape and were completely surrounded with rubber.

RUBBER AND SULFUR—It was not possible to obtain compatible results in regard to the size of the sulfur crystals in rubber, since they vary in each batch mixed. The sulfur dissolves in the hot rubber on the mills and small rhombic crystals crystallize out after the milling. It was found, however, that the average size of the sulfur crystals in rubber decreased and the coefficient of uniformity improved when sulfur of decreasing size was incorporated on the mills. The size was about 60 microns in a mixture of 100 rubber and 3.5 sulfur when ordinary sulfur was used, about 20 microns when the sulfur was sifted through a 200-mesh sieve before milling, and around 6 microns when the sulfur was ground with water for 8 hours in a ball mill, dried at low temperature, and mixed with rubber. The sulfur crystals agglomerated during milling to some extent.

RUBBER, CARBON BLACK, AND SULFUR—A mixture of 100 rubber, 1.0 carbon black, and 3.5 sulfur was selected for this investigation. There are no methods known for obtaining quantitative values for the dispersion of pigments in uncured compounds, although such values can possibly be obtained by determination of light absorption or x-ray examination. It is the intention to continue the investigation along these lines in connection with E. A. Hauser in the immediate future.

It was therefore decided to follow and record the changes that take place in this system during vulcanization. Similar studies in regard to the nature of the vulcanization process have previously been undertaken by Weber,[58] Breuil,[59] Loewen,[60] Dannenberg,[61] Pohle,[62] and Regnauld.[63] Thin, transparent layers of the compound were examined microscopically in the "Quetschkammer," and the latter was then introduced into an electrically heated oven at 140° C. for different lengths of time. After the "Quetschkammer" had cooled down to room temperature, the changes that had taken place in the rubber-pigment mixture were recorded by examination under the microscope and by taking photomicrographs, with special precautions that the same visual field and the same focal plane were examined each time. In this manner it was possible to follow the changes that took place in the system in regard to the dispersion of the pigments and to study and recognize the behavior of individual particles in relation to agglomeration and flocculation. Figure 1 shows the system rubber–carbon black–sulfur after being heated for 30 minutes at 140° C. A large sulfur crystal is disintegrating surrounded by a great number of colloidal sulfur granules which occur during the cooling down of the system. These granules have previously been studied by Dannenberg, who considers that their appearance constitutes and signifies the beginning of vulcanization—an assumption

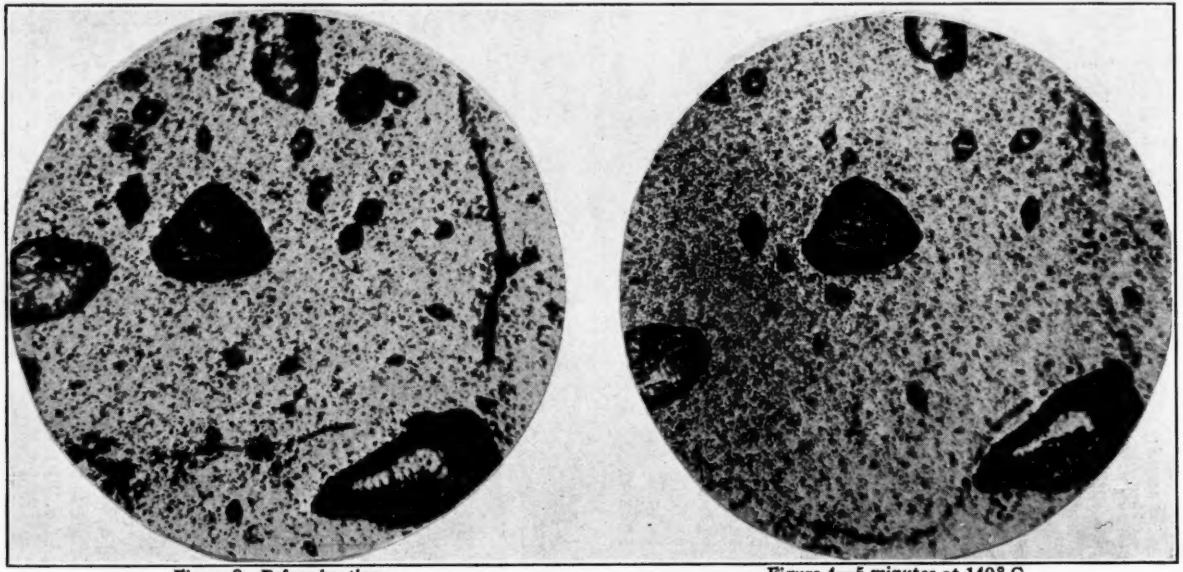

Figure 3—Before heating

Figure 4—5 minutes at 140° C.

Figures 3 to 7—Rubber–Zinc Oxide–Sulfur. 520 ×

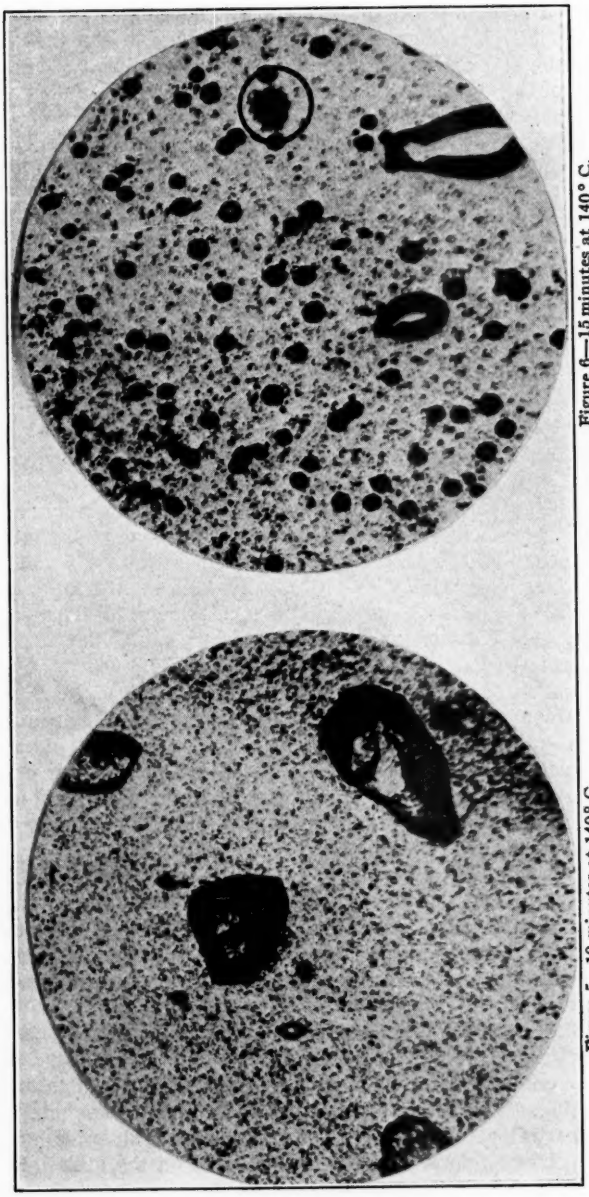

Figure 6—15 minutes at 140° C.

Figure 5—10 minutes at 140° C.

one cannot uphold according to later investigations. Figure 2 shows the same sample after reheating for 30 minutes. The sulfur crystal has now disappeared almost completely and a great number of carbon-black flocculates are noticeable, many of them not having been seen in the previous photograph and consequently were formed during the heating of the system. To take one example, we will follow the increase in size of an aggregate marked on the photograph with a circle. It shows that individual particles have flocculated around a larger nucleus increasing its size considerably.

The objection to this method of studying the behavior of pigments during vulcanization is the fact that the heating is not continuous and the rubber has a chance to cool before the changes in dispersion can be recorded under the microscope. Work is being done at the present time, however, in which the compound is cured under the microscope, using a heatable "Quetschkammer," and every step in the process will be recorded as it takes place. The results will be published at a later date.

RUBBER, ZINC OXIDE, AND SULFUR—The system 100 rubber, 2 zinc oxide, and 3.5 sulfur is shown in Figures 3 to 7. In Figure 3 we see the appearance of the system after milling. The small rhombic crystals represent recrystallization products from sulfur dissolved in rubber on the mills. Figures 4 and 5 show the system after heating for 5 and 10 minutes, respectively, at 140° C. Figures 6 and 7 are taken after heating for 15 and 45 minutes, respectively. There is a fairly good dispersion of zinc oxide in general, but several flocculates have formed during the heating. One of these flocculates is indicated in Figures 6 and 7 with a circle. In this connection we have to remember that the zinc oxide pigments are chemically active during vulcanization, and flocculation may depend to a great extent on chemical processes. One can notice particle dissolution and formation of zinc resinates when watching the cure continuously under the microscope.

RUBBER, ZINC OXIDE, CARBON BLACK, STEARIC ACID, SULFUR, AND DI-*o*-TOLYLGUANIDINE—The following basic compound was used: 100 rubber, 3 zinc oxide, 3.5 sulfur, 2 carbon black, 1 stearic acid, and 1 di-*o*-tolylguanidine; and in addition, the same mixture was studied with progressive increase of the zinc oxide up to 30 parts.

The uncured basic compound was first studied microscopically in the "Quetschkammer" and then heated for different lengths of time. Figure 8 shows the system after milling. The sulfur crystals are coated with pigment particles. One can frequently notice sulfur crystals acting as nuclei for agglomeration of carbon black on the mills. Fig-

Note—When sulfur and carbon black are milled in together, the carbon-black particles tend to agglomerate around sulfur crystals which act as nuclei. If carbon black is properly dispersed in rubber before the sulfur is added, there is not the same tendency for the black to agglomerate around sulfur crystals. Even here, however, the carbon black does tend to aggre-

gate to some extent in connection with the melting of the sulfur crystals in the hot rubber in the same way as completely dispersed carbon black forms flocculates during vulcanization.

ure 9 shows the same system after 15 minutes of heating. The sulfur crystals are melting and the rubber has absorbed large quantities of sulfur, showing a light coloration in the areas where this has taken place. After 30 minutes of heating (Figure 10), the sulfur crystals are now almost completely absorbed by the rubber. Two circles indicate flocculates evidently formed in connection with the melting of sulfur crystals.

When these compounds were cured at 45 pounds steam pressure for 50 minutes in a platen press and microscopical sections prepared, it was found that the basic compound

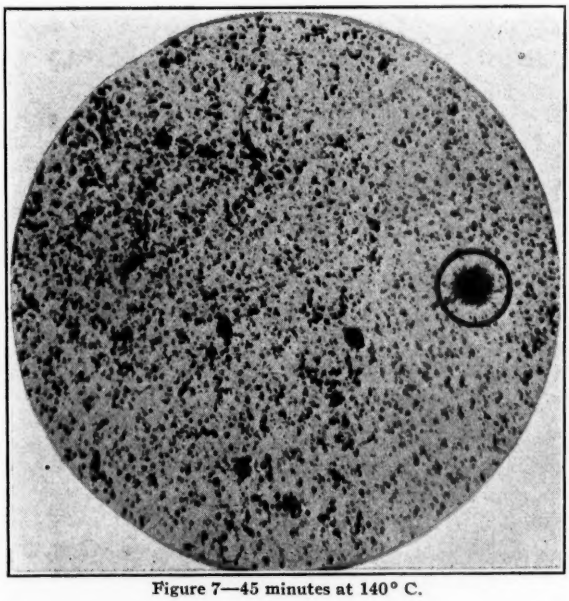

Figure 7—45 minutes at 140° C.

(with 3 parts of zinc oxide) had the best dispersion, and the higher the percentage of zinc oxide the more marked was the flocculation of the particles. Figure 11 shows the dispersion in a compound containing 10 parts of zinc oxide. The large black formation represents an aggregation of carbon black and the white spots are zinc oxide flocculates, as has been ascertained by dark-field examination. Figure 12 shows a compound containing 30 parts of zinc oxide. A carbon-black flocculate is indicated with a circle. Although these mixtures contained only 2 parts of carbon black as compared with 30 parts of zinc oxide, the flocculates of the former were in general more pronounced than those of the latter. There appears to be present an antagonistic action between zinc oxide and carbon black in regard to dispersion—i. e., the zinc

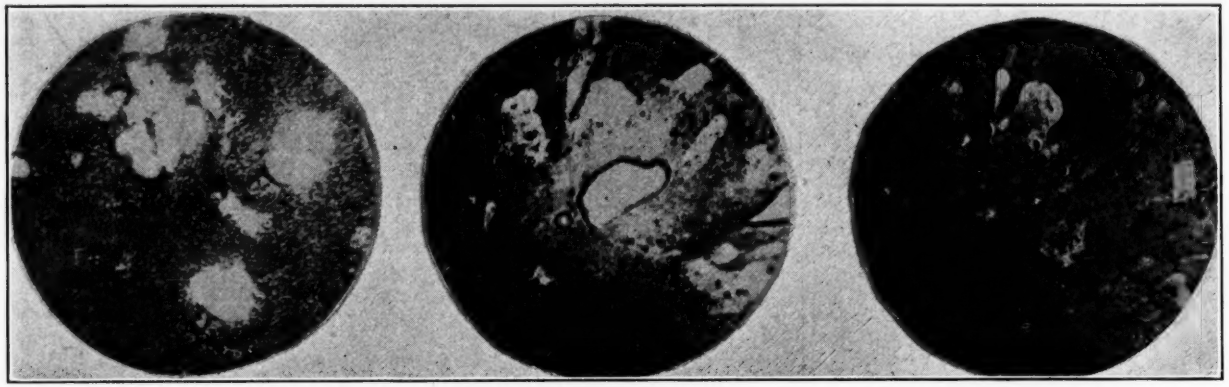

Figure 8—Before heating

Figure 9—15 minutes at 140° C.

Figure 10—30 minutes at 140° C.

Rubber–Carbon Black–Zinc Oxide–Sulfur–Stearic Acid–Di-*o*-tolylguanidine. 350 ×

oxide causes deterioration of the dispersion of the black. This may be explained by the chemically active zinc oxide changing the acidity of the rubber during vulcanization and thus affecting the degree of wetting of the inactive carbon black by the rubber.

FLOCCULATION AND DISTRIBUTION OF PIGMENTS IN HIGHLY COMPOUNDED TREAD STOCKS CONTAINING ABOUT 25 PER CENT OF CARBON BLACK—Figure 13 shows a microsection of a tread presenting a fairly good dispersion of the carbon-black particles. Figure 14 shows aggregates of carbon black in a similar compound. When these sections were examined microscopically using dark-field illumination the whole photograph was dissolved into an unorientated network, as shown in Figure 15. Owing to the complicated diffraction patterns obtained with dark-field illumination, great difficulty may be experienced in arriving at a correct explanation of the phenomena observed. The work will therefore be continued along

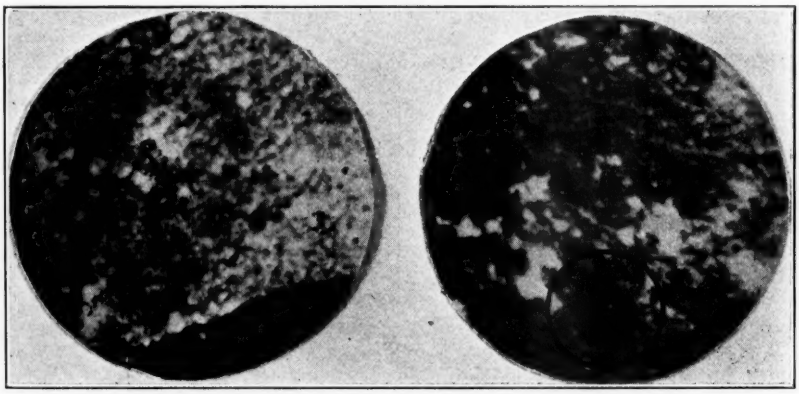

Figure 11—10 per cent zinc oxide Figure 12—30 per cent zinc oxide

Same as Figures 8, 9, and 10 except for Amount of Zinc Oxide. 1350 × and Enlarged 3 ×

these lines using polarized and ultra-violet light. This network formation seems to depend on a nonhomogenous piling of the pigment particles and should not be mistaken for a microtome effect, which is quite different and indicated by stresses and strains in the microsection. The nature of the particle piling in vulcanized rubber is of greatest importance, since it gives a measure of the surface energy present and should give us a clearer understanding of the nature of the pigment reënforcement of rubber.

Discussion

Pigments dispersed in rubber show in many instances similar behavior to dispersed particles in other systems. It has been found that agglomeration of pigment particles on the mixing mills usually takes place around any larger nuclei

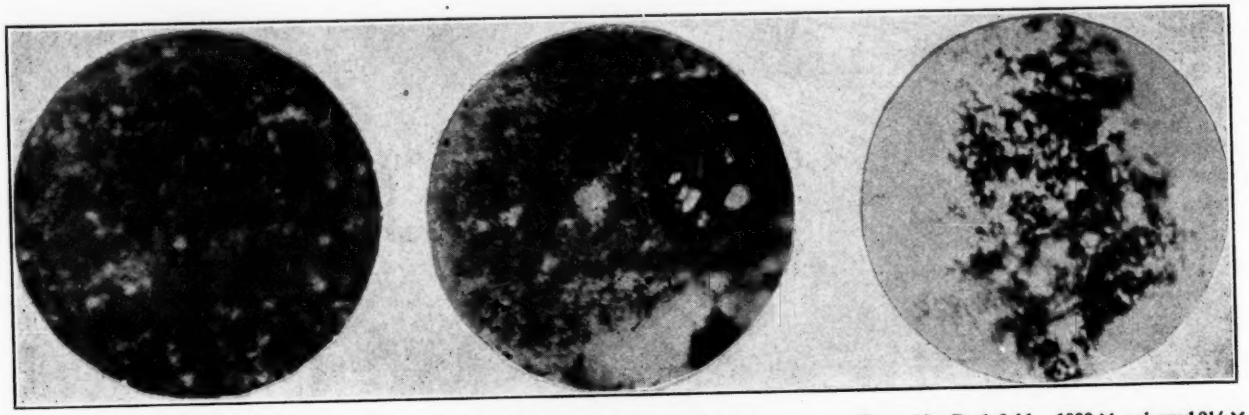

Figure 13—1300×, enlarged 3×

Figure 14—1000×, enlarged 2½×

Figure 15—Dark field. 1000 ×, enlarged 2½×

Tread Containing 25 Per Cent Carbon Black

present in the rubber, such as dust, resin, foreign matter, and even larger compounding ingredients such as sulfur crystals. There are indications of an antagonistic action between zinc oxide and carbon black in regard to dispersion. The colloidal behavior of the particles during vulcanization shows interesting features. The beginning of vulcanization, under certain circumstances, seems to be characterized by a preliminary improvement in dispersion (compare Figures 3, 4, and 5). Whether it is an actual improvement or only apparent, depending on volume increase of the rubber and change of the index of refraction of the rubber-sulfur mixture, cannot be ascertained at the present state of the investigations. Later during the cure a flocculation of previously dispersed particles takes place in connection with increased mobility of the rubber and the pigments.

This flocculation of dispersed particles takes place even in a mixture of rubber and carbon black alone on heating, although not to such a great extent as when other ingredients are present. The tendency to flocculate was most pronounced with the fine particle-sized carbon black, although the other types of blacks, such as lamp and thermatomic, showed flocculation to some extent.

The particles may draw together in more or less dense accumulations, where the surface of the particles is in contact with the rubber matrix at every point. Groups or lumps especially of carbon black are formed in connection with the incorporation or melting of large sulfur crystals. There are also cases where small agglomerates draw together during vulcanization and form larger aggregates, and other cases where agglomerates increase in size at the expense of surrounding dispersed particles.

Finally, we have the case of chemically active pigments where flocculation seems to be connected with purely chemical reactions. All internal flow in the compound, however, comes to a sudden stop at a certain stage of the vulcanization process and dispersive changes no longer occur, except during the cooling down of the system in connection with volume changes of the rubber. The carbon-black particles in highly compounded treads seem to float through the rubber in an unorientated network, which possibly is a measure of the reënforcement of the system. The forces which regulate the dispersive changes in a system rubber–pigment are of both theoretical and practical importance and will be subject for future investigations. An understanding of the subject can only be obtained with a more thorough knowledge of the structure and physicochemical properties of rubber and pigments themselves and of the nature of the vulcanization process.

Acknowledgment

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Effect of Various Types of Carbon Black on Certain Physical Properties of Rubber Compounds[1]

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The effect of various types of carbon black on the rate of cure, tensile properties, aging, and abrasion loss of rubber has been determined. It has been found that the presence of different amounts of oxygen adsorbed on or combined with the black retards the rate of cure in direct proportion to the amount of oxygen present and decreases the maximum physical properties obtainable from a given stock. The aging data show that the higher the amount of oxygen on the black the more rapid the deterioration of the rubber stock when aged at 70° C. in air. Other physical properties such as oil adsorption, iodine adsorption, acetone extract, or color value could not be correlated with the effect of these blacks on the curing characteristics of rubber compounds.

IT IS well known to rubber technologists that different shipments of carbon black vary in their reënforcing value and in their effect on rate of cure. The cause of this variation has not been determined precisely as yet, although several investigators have offered tentative theories. John-

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

son[2] recently showed that the variation in color value could be correlated with reënforcing value in rubber if the samples of blacks came from the same plant, while no relationship was observed between these two properties if the blacks were produced at different plants. On the other hand, Twiss and Murphy[3] thought that the differences in the rate of cure of various types of carbon black were due to the adsorption of more or less of the natural accelerator from the rubber (an unaccelerated stock was used). However, Spear and Moore[4] have shown that there is no general relationship between stiffening effect in rubber and adsorption of acid or basic dyes from either water or benzene, and have shown further that there is no relation between adsorption and rate of cure. Another possible cause of the retarding effect of carbon black on the rate of cure of rubber compounds would be the presence of acidic intermediate decomposition products from the natural gas. However, no results reported in the literature substantiate this conclusion and, as will be shown later, no measurable differences in the acidity of water extracts of blacks could be noticed.

In view of the importance of the effect of carbon black on the aging of rubber compounds, it is surprising that no study of the comparative aging effect of various types of carbon black has been published. Ruby and Depew[5] showed that a stock containing carbon black aged more rapidly than one containing zinc oxide and thought that this difference was due to the oxygen adsorbed on the carbon black being activated by the carbon black itself sufficiently to oxidize the rubber. The results obtained by Tener, Smith, and Holt[6] on the comparative aging of stock containing whiting and carbon black are inconclusive because several other factors such as amount of sulfur, accelerator, and softener were changed at the same time. In view of these uncertainties it was decided to investigate this question more completely.

Relation between Physical Properties of Blacks

In an exhaustive study of carbon blacks from various sources, Neal and Perrott[7] found that the ultimate composition of these blacks was approximately the same except for the oxygen content. The data presented by these authors show that the per cent oxygen combined with or adsorbed on the black varies inversely with the calorific value within an average deviation of ±100 B. t. u., or 0.7 per cent.

Table I gives a summary of certain physical properties of different types of carbon blacks which were used in the present tests. The ink black is a standard product made by the incomplete combustion of natural gas in the channel or disk

[2] *India Rubber World*, **78**, 65 (1928).
[3] *J. Soc. Chem. Ind.*, **45**, 121 (1926).
[4] IND. ENG. CHEM., **18**, 418 (1926).
[5] *Ibid.*, **12**, 1155 (1920).
[6] Bur. of Standards, *Tech. Paper* **342** (1927).
[7] Bur. Mines, *Bull.* **192** (1922).

process; the M black is a standard channel black for use in rubber; the B black is made by a slightly modified channel process; the D and G carbons are made by the combustion of natural gas in special types of apparatus; while the lampblack, acetylene black, and thermatomic black are standard commercial products manufactured, respectively, by the incomplete combustion of oil residues or acetylene and by the cracking of natural gas. These data show that the oxygen content of the different types of blacks varies between 1.2 and 10.7 per cent. These values were obtained from the heating value of the blacks by comparison with the straight line obtained by plotting B. t. u. *vs.* oxygen content (from Neal and Perrott's data). It will be seen that the per cent oxygen shows no relationship to the iodine adsorption, the oil adsorption, the acetone extract, or the specific gravity. The only property which varies regularly with the oxygen content is the ease of oxidation. This determination was made by heating an acidified 0.02 *M* solution of potassium permanganate to 70° C. with 1 gram of black for 15 minutes and titrating the excess permanganate with sodium oxalate. It is probable that part of the oxygen is combined with carbon to form partially oxidized compounds and these compounds are more easily oxidized than pure carbon itself. The data given in this table bear out this conclusion in a qualitative manner. Another interesting fact brought out is the difference in the ratio of iodine adsorbed to the linseed oil adsorbed. For example, this ratio is 0.07 for lampblack and 0.54 for ink black. This eightfold difference emphasizes in a very striking manner the specificity of adsorption phenomena.

Table I—Physical Properties of Carbon Blacks Studied

Black	Iodine Adsorption	Oil Adsorption	Calorific Value	Acetone Extract	Oxidized by 0.02*M* $KMnO_4$	Oxygen	Sp. Gr.
	Mg./g.	*Cc./100 g.*	*B. t. u.*	%	%	%	
Ink	79.1	146	12,810	0.36	70.6	10.7	1.88
B	8.0	150	13,480	0.30	...	7.1	1.76
M	57.4	140	13,825	0.30	43.5	5.3	1.73
Lampblack	9.2	130	13,820	0.84	28.5	5.3	1.73
Acetylene	42.7	325	14,310	0.36	26.8	2.6	1.84
D	3.1	100	14,540	0.3	...	1.3	1.82
G	22.2	100	14,550	0.5	9.9	1.2	1.82
Thermatomic	6.1	46	14,550	0.5	7.7	1.2	1.84

Study of Properties of Rubber Compounded with Various Blacks

Since it was found that the various physical properties of the different types of blacks did not vary in the same manner, it was decided to determine if possible what property or properties could be used as a criterion to judge the suitabilty of a certain black for use in rubber. In the first series of tests the following compound was used: 100 parts pale crepe, 5 zinc oxide, 3 sulfur, 1 stearic acid, 25 of black, and varying amounts of Grasselerator 808, to give as near as possible the same time of cure. All samples were cured in a paraffin bath regulated

at 140° ± 0.50° C. and tested in accordance with the recommendations of the physical testing committee of the Rubber Division of the AMERICAN CHEMICAL SOCIETY except for the constant temperature and humidity control of testing room. It was found that the ink black required 2 per cent of accelerator, the M black and lampblack 1.5 per cent, and G black, thermatomic and acetylene blacks 0.5 per cent. The data for modulus at 500 per cent elongation, tensile at break before and after aging 4 days in a hot-air oven at 70° C. are given in Table II.

Table II—Effect of Blacks on Properties of Rubber Compounds Containing Them

BLACK	MODULUS AT 500% ELONGATION			TENSILE AT BREAK			EFFECT OF AGING 4 DAYS AT 70° C.	
	Minutes' Cure			Minutes' Cure			% of original tensile (50-min. cure)	% of original abrasion (40-min. cure)
	40	50	60	40	50	60		
	Kg. per sq. cm.			*Kg. per sq. cm.*				
Ink	118	140	183[a]	185	211	240[a]	41[a]	68[a]
M	197	205	201	310	303	284	57	70
G	181	183	187	254	243	241	72	76
Lampblack	183	185	192	233	222	218	66	78
Acetylene	184	185	188	250	233	235	92	90
Thermatomic	177	184	180	220	206	196	100	92

[a] 80-minute cures.

It will be seen that all the blacks except the ink-making black reach their maximum physical properties in 50 minutes while this black required 80 minutes to reach its maximum properties. It is evident, therefore, that the presence of large amounts of oxygen on the carbon retards the rate of vulcanization of the rubber. The acetylene black is the only one that is at all out of line, since according to its oxygen content it should give a slower curing compound than either G black or thermatomic, while it is found to give exactly the same curing time. The aging data show that as more oxygen is carried into the rubber compound with the black the stock ages much more rapidly. Again this relationship holds true for all the blacks except acetylene, which gives better aging stocks than blacks containing less oxygen. This difference might be due to the presence of intermediate decomposition products, although the acetone extract is only 0.36 per cent.

In order to test this point, the acetylene black was extracted with acetone and this extract was added to an equal weight of M black. These two treated blacks were milled in rubber and aging tests were made on these stocks. It was found that this treatment had not improved the aging characteristics of the M black nor decreased those of the acetylene black. At present no satisfactory explanation for the superior aging of acetylene stocks can be offered.

The abrasion resistance of these compounds as determined by means of the Grasselli abrader[8] before and after aging

[8] Williams, IND. ENG. CHEM., **19**, 674 (1927).

shows that the deterioration as measured by this test has not been so great as decrease in tensile at break. This difference is due to the fact that the abrasion tests were run for 10 minutes whereas if they had been run for only 2 minutes the loss would have been considerably higher, since the deterioration of the surface of the blocks is greater than at the center owing to the action of oxygen on this surface layer. (For a more complete discussion of the abrasion loss of aged stock, see paper by Plummer and Beaver.[9])

Effect of Oxygen Content of Black

In order to determine more precisely the effect of the amount of oxygen in the black on the physical properties of the rubber compound, a series of mixtures of ink black and M black was made using the following formula: 100 parts pale crepe, 5 zinc oxide, 4 sulfur, 1 stearic acid, 25 black, 0.75 diphenylguanidine. The data are given in Table III and show that the tensiles at break of the 140-minute cure of these stocks fall on a straight line. Since the amount of oxygen carried into the rubber mixes by the blacks varies in a continuous manner, it is evident that the physical properties as measured by the tensile at break vary inversely as the per cent oxygen on the blacks. Plotting the modulus at 500 per cent elongation brings out this same relationship, showing that the rate of vulcanization is also proportional to the amount of oxygen on the black. The aging data on this series of compounds are not given, since the stocks containing high percentages of the ink black are so undercured that they show no indication of the actual aging characteristics of the black.

Table III—Relation between Oxygen Content of Mixtures of Ink Black and M Black on Properties of Rubber Compounds
(140-minute cure at 140° C.)

Black		Modulus at 500% Elongation	Tensile at Break	Oxygen on Black
Ink	M			
%	%	*Kg. per sq. cm.*	*Kg. per sq. cm.*	%
100	0	50	94	10.7
75	25	77.5	115	9.4
50	50	114	158	8.0
25	75	148	184	6.6
0	100	169	207	5.2

Another possible explanation of the data presented here is that the differences in the tensile or modulus figures are due to the difference in the reënforcing properties of the black and not to the retarding effect of the oxygen on the rate of cure. However, the data in Table II show that with sufficient accelerator present the ink black will give a stock with as high a modulus and tensile as that of the M black. That the adsorptive characteristics of the blacks are not responsible for the differences in the rate of cure can be seen from Table I. For example, lampblack adsorbs only 21.5 per cent as much iodine and 40 per cent as much linseed oil as acetylene black,

[9] Subsequent issue, Ind. Eng. Chem.

but requires about three times as much accelerator to give the same rate of cure. On the other hand, the ink black adsorbs 38 per cent more iodine than the M black and requires somewhat more than 33 per cent accelerator to give it the same time of cure. However, its oil adsorption is only 4 per cent greater than the M black. It seems reasonable to conclude that adsorption of iodine or linseed oil does not indicate the curing characteristics of the black. Therefore, it can be concluded that the differences noted above are due to the presence of the oxygen in the black.

Further confirmation of this conclusion is given in Table IV. These data were obtained with the same test formula used for the ink black–M black mixtures, and show that the properties of compounds containing mixtures of G and M blacks also vary in a continuous manner. Since the difference in the amount of oxygen on these two blacks is not so large as it was with the previous mixtures, the slope of the modulus curve is smaller. Another interesting point brought out in this test was the effect of the increased amount of oxygen on the rate of deterioration of the stock. It was found that the higher the amount of oxygen carried in the stock by the black the more rapid the deterioration, although this deterioration was only approximately a direct function of the amount of oxygen present.

Table IV—Relation between Oxygen Content of Mixtures of G and M Blacks on Properties of Rubber Compounds
(100-minute cure at 140° C.)

Black		Modulus at 500% Elongation	Tensile at Break	Oxygen on Black	% of Original Tensile, Aged 4 Days at 70° C. (Best Cure)
G	M				
%	%	*Kg. per sq. cm.*	*Kg. per sq. cm.*	%	
0	100	165	298	5.2	20
25	75	183	288	4.2	25
50	50	198	269	3.2	33
75	25	222	269	2.2	59
100	0	232	248	1.2	66

Table V—Effect of Various Blacks on Time of Cure

Black	Time of Cure at 140° C.	Modulus at 500% Elongation	Tensile at Break	% of Original Tensile, Aged 6 Days at 70° C.
	Minutes	*Kg. per sq. cm.*	*Kg. per sq. cm.*	
B	160	169	288	9
M	160	191	304	10
G	100	220	274	26
D	100	223	273	26
Acetylene	80	219	250	45
Lampblack	140	113	201	8
Thermatomic	120	113	225	35

Another series of tests was made using the same amount of accelerator and changing the time of vulcanization to give the maximum physical properties. The compounds used for this test contained 100 parts of pale crepe, 5 zinc oxide, 4 sulfur, 1 stearic acid, 25 of black, and 0.75 diphenylguanidine. These results (Table V) again show the very great difference in the rate of vulcanization of compounds containing the same amount of black but different amounts of oxygen and also show the difference in the maximum physical properties produced under these conditions. It will be seen that the

data agree very well with those presented previously. The figures for the ink black are omitted, since it was too much under-cured to give satisfactory results. The more rapid deterioration of these stocks compared with those shown in Table II is due to the fact that diphenylguanidine does not have so great an antioxidant action as Grasselerator 808.

Conclusion

The data presented herein show that in general the presence of oxygen on carbon black retards the rate of vulcanization in direct proportion to the amount of oxygen present and also decreases the maximum physical properties obtainable with a given amount of accelerator. The aging data show that the presence of this oxygen on the black increases the rate of aging as the amount of oxygen increases, but not in direct proportion to the per cent of this oxygen present. It can be concluded, therefore, that compounds which contain a small amount of oxygen, such as thermatomic, G black, or acetylene black, will give better aging stocks than compounds containing higher amounts of oxygen such as lampblack and standard channel blacks. No correlation could be found between the acetone extract, iodine adsorption, or oil adsorption, and the effect of these blacks on the rate of cure or aging.

Acknowledgment

The authors wish to express their appreciation to the Combustion Utilities Corporation for permission to publish these results and to C. J. Wright, chief technologist of this company, whose interest and support have made it possible to carry on this work. The coöperation of Ira Williams, of the Grasselli Chemical Company, is also gratefully acknowledged.

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Abrasion Tests of Rubber Stocks Containing Various Types of Carbon Black[1]

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The abrasion loss of rubber stocks containing different types of carbon black was determined by means of the Williams abrasion apparatus. It was found that the abrasion loss per unit of work increased as the size of the abrasive increased up to 0.45 mm. and then decreased quite rapidly. No adequate explanation for these results has been found. It was shown further that the ratio of the abrasion loss of unaged stocks containing various types of carbon black to these stocks after aging in the Geer oven was not constant, since it was found that some types of carbon black increase the rate of deterioration of rubber much more than other types.

THIS paper presents certain interesting results obtained during the course of a general study on the abrasion resistance of rubber stocks compounded with various types of carbon black. All tests have been carried out using the Grasselli abrasion tester as described by Williams,[2] since this method measures the actual power consumed per unit of material abraded, and hence eliminates some of the un-

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

[2] IND. ENG. CHEM., **19**, 674 (1927).

certainties inherent in other abrasion test devices. Vogt[3] has tested seven reclaim stocks by this method as well as with four other devices, all designed to measure or take account of the power consumed during abrasion. Averaging the results of three of his methods, the fourth being definitely discordant with the others, the relative abrasion resistances for the various stocks were 100-95-91-83-80-74-71, whereas with the Grasselli abrasion machine the results were 100-91-89-83-77-72-67. The concordance between these results is very close. In his second paper Vogt discusses certain differences between the results of his "angle abrasion" machine and the Williams machine, to which further reference will be made later.

In the present tests with the Grasselli machine the standard procedure outlined by Williams has been used except that round blocks are used instead of square ones. This simplifies the construction of molds very greatly and permits test blocks to be made by rolling up narrow strips of the raw stock, which completely eliminates any possible effect of calendar grain on the test results and in general gives a more satisfactory test block. Check determinations have shown no difference in results between round or square blocks.

The average deviation of test results for a given stock by this method has been found in general to be less than 3 per cent, although occasionally a given test will give obviously discordant results, ordinarily in the direction of low abrasion loss. A priori this might result from changes in the motor speed (line voltage), in the size of the abrasive, or in the condition of the abrading or abraded surface. No detectable differences in speed have been observed during tests, and although the abrasive size is important, as discussed later, it cannot account for the occasional erratic results. Such results are attributable only to the condition of the surface involved, and hence in routine testing special attention should be paid to cleaning the surface of the test blocks with a cloth moistened with benzene, to insuring the absence of entrained oil in the air blast used for keeping the paper clean, and to avoiding the presence of accidental oily or greasy impurities on the surface of the abrasive paper.

Effect of Size of Abrasive

Williams states, "It is improbable that the work required to remove a given volume of rubber as fine particles would be the same as that required to remove an equal volume as large particles. In order to secure uniform results, fresh paper should be used for each test." The present writers' results have shown not only that it is necessary to use fresh paper for each test, but that the results are a definite function of the size of the abrasive, as shown in Figure 1. Compound "A" consists of 100 parts pale crepe, 5 zinc oxide, 4 sulfur, 1 stearic acid, 0.75 diphenylguanidine, 25 black, the

[3] IND. ENG. CHEM., **20**, 140, 302 (1928).

cure at 140° C. being 120 minutes for black "M" and 80 minutes for black "G." Compound "C" is a highly compounded stock containing 100 pale crepe, 5 zinc oxide, 5 sulfur 1.5 D. P. G., 60 black, cure at 140° C. for black "M" 75 minutes, for black "G" 45 minutes. The figures near the arrows at the bottom of the graph refer to the size number of standard emery paper used. The points marked "Saw" refer to a special abrasive surface made by coiling tightly a 0.47-cm. ($^3/_{16}$-inch) metal-cutting band saw and soldering it to a brass plate. The average particle size of the various papers was determined by microscopic examination, using an ocular micrometer and measuring a large number of particles.

It will be observed that up to a particle size of about 0.45 mm. the results fall accurately upon lines having the slope of 0.67. This shows definitely that with varying abrasive size the volume loss per unit of work done is proportional to the new surface generated per volume removed, since for spherical particles surface is a function of the $^2/_3$ power of volume. It is rather surprising that this relation should hold so accurately, since the shape of the particles removed by abrasion is shown by microscopic examination to be long and stringy, rather than in any way spherical. The results observed for abrasive sizes over 0.45 mm. are still more surprising, particularly with respect to the suddenness of the break in the curves. Apparently, with the larger abrasive sizes new and unknown factors come into play or a new balance is set up between effective abrasive work and work lost in friction. The data shown have, however, been confirmed by numerous check determinations which are not shown. It is also interesting to note the results obtained using the side of an ordinary 30- to 40-mesh carborundum grinding wheel in place of the abrasive paper, the loss for blacks "G" and "M" (compound "A") being, respectively, 260 and 208 cc. per kilowatt-hour. Using no abrasive but merely running the blocks against the machined surface of the brass supporting disk, a small but appreciable loss was obtained, respectively, 9.3 and 7.4 cc. per kilowatt-hour.

Energy Consumption in Abrasion Tests

The total power consumption during abrasion tests, as measured in a machine of the present type, is surprisingly near to constant for given conditions of load on the test pieces, speed of the abrasive surface, etc., regardless of the actual abrasion loss of the stock under test. Vogt has found this to hold very closely with his angle abrasion machine, but finds less constancy in his tests with the Williams machine. Of the tests reported herein, for example, the actual rate of work during the tests of the various stocks of Table I lay between 11.8 and 12.1 watts, although the abrasion loss varied from 254 to 430 cc. kilowatt-hours. For the tests of Table II the power consumption was 12.1 to 13.2 watts for abrasion losses of 299 to 464 cc. per kilowatt-hour but was 14.3 watts

for the lampblack stock and considerably higher for the undercured stock with "ink-making" black. Of the results with various sizes of abrasive paper shown in Figure 1, for compound "A," black "M," the power decreased from 14.2 to 11.6 watts with increasing abrasive size, for compound "A," black "G," from 13.1 to 11.1 watts similarly. With the highly compounded stock "C," black "G," the power consumption was 10.7 to 10.5 watts.

As pointed out by Vogt, this relative constancy of power consumption indicates that only a small percentage of the power input goes to do true abrasive work. He supports this by calculations showing that the power consumption of abrasive test machines of the present types represents 35 to 120 times the energy input per cubic centimeter of rubber removed as would be necessary to disintegrate 1 cc. by stretching. This value he determines based on the conception that a piece of rubber "superstretched" above its normal break until its energy of resilience is 50 per cent greater than normally possible will disintegrate to a powder on rupture instead of a single break. This calculation, however, neglects the fact that a tremendously greater amount of new surface is produced in the first case, which, as shown by the present tests (Figure 1), is an important factor. On the other hand, if we assume that the ordinary tensile rupture of 1 cc. of rubber produces 1 sq. cm. of new surface, and if we therefore multiply his value for the energy of rupture by the amount of surface generated in abrading 1 cc. to, for example, 0.2 mm. cubical particles, we find that this new figure is much greater than the total measured energy consumption during abrasion. This may be taken to indicate that removing small particles by abrasion is more of a tearing than a tensile phenomenon, since resistance to tear is always lower than the ultimate strength in pure stretching.

To consider another aspect of this matter briefly, it is difficult to conceive of any major points of consumption of energy in the Williams machine save actual abrasive work and heat generated by friction between the rubber and abrasive or as result of hysteresis of the specimen. If we assume that 90 per cent of the total heat generated is dissipated into the testing machine or the air, and take Williams' figure of 7° C. as the final temperature rise of the (10-gram) test blocks at the end of a typical 20-min. test, the total energy liberated as heat throughout the test would not be more than 10 to 20 per cent of the observed input. On the other hand, when running test blocks of compound "A" (blacks "M" and "G") against the bare machined brass wheel of the Williams machine, the tests showed an abrasion loss of only 7 to 9 cc. per kilowatt-hour, but the power consumption was 17.0 to 17.1 watts. This is actually much higher than for normal abrasion tests, and shows the magnitude which it is possible for thermal losses in a machine of this sort to attain under certain circumstances.

Unfortunately, however, the consideration of the fore-

going facts leads mainly to the conclusion that there is much to be learned about the mechanism of abrasion before the testing machines and methods will be entirely understood and satisfactory.

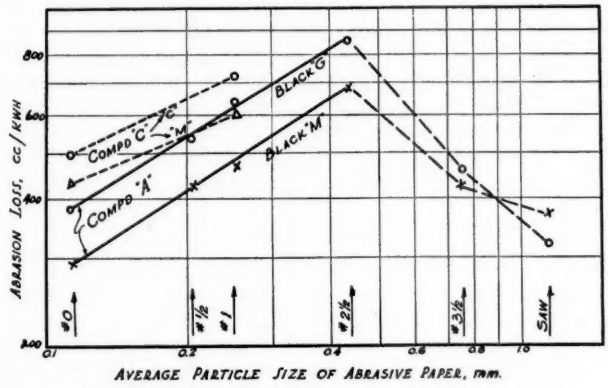

Figure 1—Abrasion Resistance *vs.* Abrasion Size

Abrasion Resistance of Stocks Containing Various Carbon Blacks

Various carbon blacks have been compared by two methods with respect to their abrasion characteristics when compounded in rubber. In the first series of tests Grasselerator 808 was used as accelerator, the amount of which was varied to compensate for the different curing characteristics of the blacks, while in the second series a constant amount of accelerator (diphenylguanidine) was used in all compounds. The blacks used included "ink-making" black, as prepared from natural gas by the channel process as regulated with view to the requirements of the ink trades; black "M," a standard gas black as prepared by the channel process for the rubber trade; black "G," a black prepared by the combustion of natural gas in a special type of apparatus. Acetylene black, lampblack, and Thermatomic carbon are products requiring no further identification for present purposes.

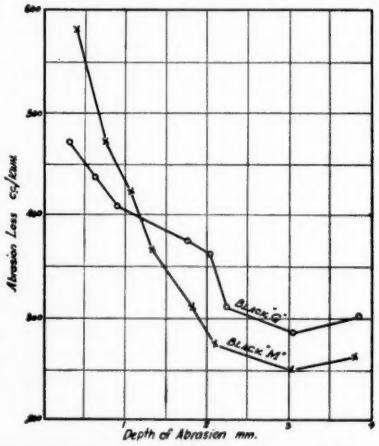

Figure 2—Compound "A" Aged 4 Days at 70° C.

Series 1—The results for this series are shown in Table I.

The adjustment of the accelerator was such as to give stress-strain curves of the same shape, or in other words with maximum cure at 40 to 50 minutes for all blacks except the first one tabulated, which is not used in rubber compounding but is given as of general interest. The compound with this black was obviously greatly overaccelerated in order to cure it at all. The results for the other blacks are in line with general knowledge, but are nevertheless interesting as a summary comparison. It will be noted that in general the blacks having the lower initial abrasion loss show the greatest percentage degradation on aging and vice versa, although acetylene black is somewhat of an exception to this rule.

Table I—Abrasion Resistance Data. Series 1

Formula: 100 pale crepe, 5 zinc oxide, 3 sulfur, 1 stearic acid, 25 black, accelerator as noted

Type of Black	Grasselerator 808	Cure at 140° C.	Modulus at 500%	Ultimate Tensile	Abrasion Loss Before aging	Abrasion Loss Aged 4 days[a]	Ratio Aged/Normal
		Min.	*Kg./sq. cm.*		*Cc./kw-hr.*		
Ink-making black	2.0	80	41	239	306	447	0.68
Gas black "M"	1.5	40	197	310	254	362	0.70
Gas black "G"	0.5	40	183	253	296	392	0.76
Lampblack	1.5	40	180	221	430	487	0.88
Acetylene black	0.5	40	184	250	329	366	0.90
Thermatomic carbon	0.5	40	101	205	430	465	0.92

[a] Aged in Geer oven at 70° C. and the abrasion test blocks run 10 minutes under standard conditions with the removal of approximately 2 mm. of surface stock, as distinct from the tests shown in Figures 2 to 7, which were run for 2 minutes only with the removal of approximately 0.4 mm. of stock.

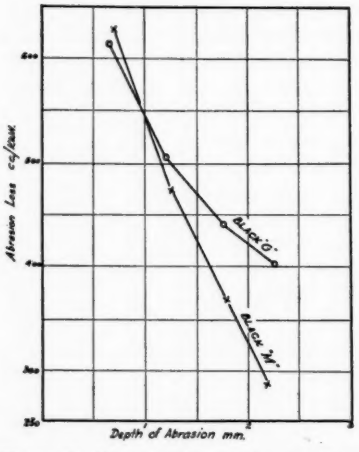

Figure 3—Compound "A" Aged 6 Days at 70° C.

Series 2. The formula used and the results for the second series of compounds are shown in Table II. The stock containing "ink-making" black is again obviously out of line, being greatly undercured even at 140 minutes. Differences in the reënforcing power of the blacks are more noticeable here than in Table I. The fast-curing (non-retarding) blacks, "G" and acetylene, show the highest stiffening effect, although black "M" definitely has the highest ultimate strength. The abrasion results are in the same general order as in the first series of tests.

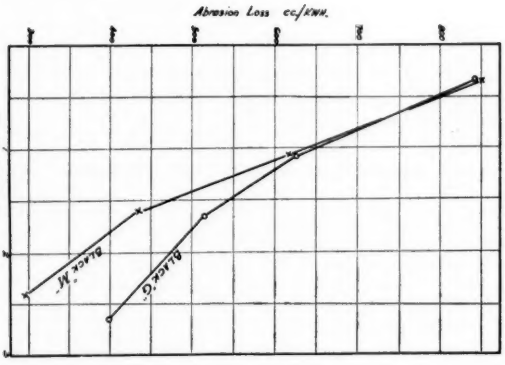

Figure 4—Compound "A" Aged 10 Days at 70° C.

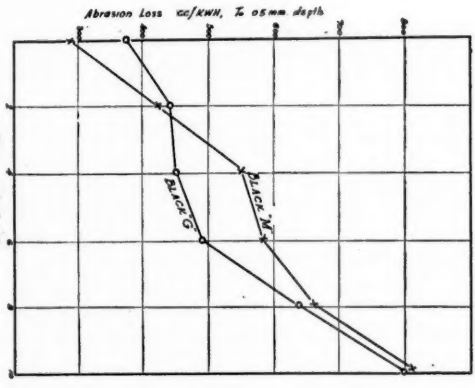

Figure 5—Surface Abrasion Loss vs. Aging Time—Compound "A."

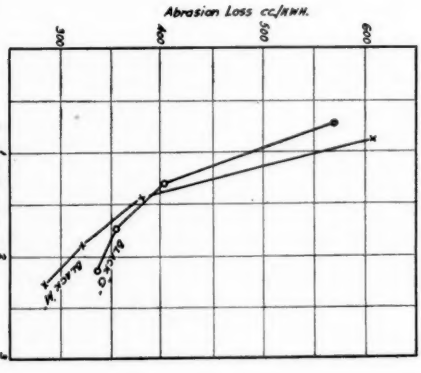

Figure 6—Compound "B" Aged 4 Days at 70° C.

Table II—Abrasion Resistance Data. Series 2

Type of Black	Cure at 140° C.	Modulus at 500%		Ultimate Tensile		Abrasion Loss
	Min.	*Kg./ sq. cm.*	*Lbs./ sq. in.*	*Kg./ sq. cm.*	*Lbs./ sq. in.*	*Cc./ kw-hr.*
Ink-making black	140	70	1000	95	1330	810
Gas black "M"	100	183	2600	302	4300	299
Gas black "G"	80	211	3000	243	3450	380
Lampblack	80	95	1320	184	2610	576
Acetylene black	80	218	3100	244	3470	416
Thermatomic carbon	80	98	1400	228	3250	464

Effect of Aging on Abrasion

The use of the Grasselli abrasion machine permits the study of the abrasion resistance of aged stocks during the removal of progressive small increments of material from the surface inwards. The test is carried out under standard conditions, except that a large number of two-minute runs are made in series instead of one longer run, the blocks being always replaced in the same position with respect to the direction of abrasion as shown by the friction marks. If the abrasion loss for a series of such tests is plotted *vs.* the total cumulative depth of abrasion as calculated from the cumulative total weight removed, the results are interesting. For the test stock compound "A" these results are shown in Figures 2 to 4, where the normal loss for the unaged stocks with blacks "M" and "G" is, respectively, 290 and 375 cc. per kilowatt-hour. It will be observed that for all aging periods this relation is reversed for the first millimeter of stock from the surface, black "M" now showing the higher abrasion loss. With an aging period of 8 days, but more particularly at 10 days, the degradation of the rubber is so complete that the differences in the surface layer, owing to the type of carbon black used, are much less pronounced than at an aging period of 4 days. In Figure 5 for compound "A" the abrasion loss for the surface layer has been plotted against aging time. In order to give a constant basis of comparison the abrasion loss has been read from the various individual curves as that loss indicated at a cumulative total of 0.5 mm. depth of abrasion. Here it will be seen that after 2 days' aging the relative abrasion loss of the compounds with

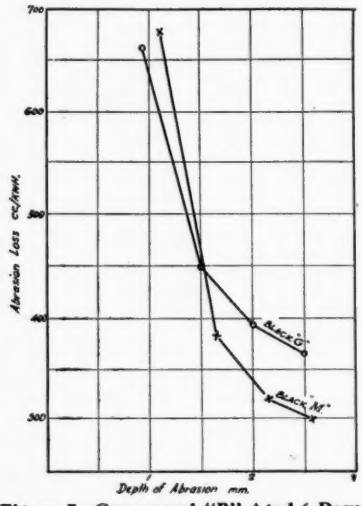

Figure 7—Compound "B" Aged 6 Days at 70° C.

the two blacks is reversed, although at and after 8 days the general surface degradation is so great that the results are practically indistinguishable. There is no particular evidence from this curve of the existence of any induction period in aging such as has been found by various authors, although it might be perceptible at shorter aging periods.

That the effect of the type of carbon black on aging is not restricted to one particular compound or accelerator is shown by Figures 6 and 7 for compound "B," whose formula was 100 pale crepe, 5 zinc oxide, 3 sulfur, 1 stearic acid (25 black "M," 1.5 No. 808) or (25 black "G," 0.5 No. 808) both cured 40 minutes at 140° C. The normal abrasion of the unaged stocks of compound "B" for blacks "M" and "G," respectively, was 254 and 296 cc. per kilowatt-hour. It will be seen that here also, as with compound "A," the relative abrasion resistance in the surface layer of the compounds with the two blacks is reversed after aging.

It might be expected that curves such as the foregoing would give a definite index of the rate of penetration of oxygen into the stock on aging. Consideration of the curves, however, shows that the reactions occurring are too complex to permit this. For example, in Figure 2 black "G," having a normal resistance (unaged) of 375 cc. per kilowatt-hour, after 4 days at 70° C. the abrasion loss in the middle of the block (2.5 to 4.0 mm.) is only 300 cc. per kilowatt-hour, showing that there has been considerable improvement due to aftercuring. The cures used in all these abrasion tests were 10 to 15 minutes below the maximum cure as indicated by the modulus at 500 per cent elongation. The Geer oven test at 70° C. has been compared unfavorably by some to the oxygen-bomb test, being claimed to give results more influenced by purely thermal deterioration from the long exposure at an elevated temperature, rather than resulting from the actual reaction of oxygen on the rubber. The data of the present tests show conclusively the deterioration to be progressive from the surface inwards, which obviously can be done only to the action of oxygen, since there is no appreciable thermal deterioration in the interior of the block, but rather as noted above, a definite improvement due to aftercuring. It should perhaps be emphasized that the stiffening of stock due to overcuring will not improve the abrasion results on a testing machine of the present type, which measures abrasion per unit of work done. The fact is, however, that the curves as obtained represent the resultant effect of two changes—first, a certain actual improvement due to aftercuring; and second, the deterioration from the surface inwards due to oxygen penetration, which precludes their giving any accurate data as to the rate of such penetration.

Conclusion

With respect to the results noted herein on the relation of abrasion loss to size of abrasive material, it is regretted

that as yet no results have been obtained which cast much light on the reasons for the break in the curves of Figure 1. It is possible, if not probable, that the unexpected phenomena whose existence is indicated by these results may be responsible for the commonly observed discrepancies between laboratory abrasion tests and road tests. It is hoped that further studies may give more useful information on this relation.

The abrasion results on aged stocks present several important points. It is, of course, obvious and fully realized that abrasion in use takes place only on the surface layer of a tire tread, but attention has not before been called to the very considerable effect which the aging characteristics of the carbon black used in the stock may have on the abrasion resistance of this surface layer. The present results show that, with two stocks differing only in their carbon black content, the relative abrasion resistance of the surface layers after aging may be in reversed ratio to those of the unaged stocks. This evidently will be a decisive factor in the relative useful life of the tread if the rate of surface aging is greater than the rate of tread wear. Surface conditions or, in other words, the time of storage before use, the daily mileage, existing road and climatic conditions, etc., will determine this relation.

Acknowledgment

The authors wish to express their appreciation to the Combustion Utilities Corporation for permission to publish these results, and to C. J. Wright, chief technologist of this company, whose interest and support have made it possible to carry on this work. The coöperation of Ira Williams, of the Grasselli Chemical Company, is also gratefully acknowledged.

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Carbon Blacks and Their Use in Rubber[1]

III—Aging Effects

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This is a continuation of work previously presented on the comparison of various properties of carbon blacks. Part I[2] discussed the characteristics of the blacks themselves and their behavior in uncured rubber. Part II[3] described their action when compounded in cured rubber stocks containing various accelerators. The present article is a discussion of the effects of aging on various properties of the same base mix of rubber and sulfur with the same carbon blacks and accelerators.

THE comparative effect of a number of pigments upon the aging of rubber has been set forth by Vogt.[4] The present investigation has been designed to give more extensive data covering a narrow field—the effect of various carbon blacks on rubber aging. The stocks have been aged for 18 months in a dark cabinet with slow air circulation. The temperature was the average room temperature which was probably near 65° F. (18° C.). The tensile tests were made upon the remainder of the sheet from which the original tests were made. The hardness and abrasion tests were made upon the original test pieces.

No accelerated age tests were made because, as has been

[1] Received May 29, 1928.

[2] Goodwin and Park, IND. ENG. CHEM., **20**, 621 (1928).

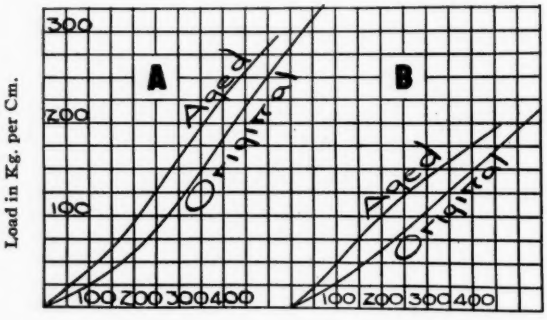
[3] *Ibid.*, **20**, 706 (1928).

[4] *Ibid.*, **17**, 870 (1925).

pointed out elsewhere,[5] one of the authors does not feel convinced that the methods now in vogue accurately represent the changes which occur during natural aging of tire stocks.

Hardness

The hardnesses of the aged stocks, as obtained by the Shore durometer, do not show any great deviation from the originals. All stocks are about 5 to 20 per cent harder than the originals and there is no regularity in behavior which separates one black from another. The diphenylguanidine stocks have hardened to a slightly less extent than the others.



A—30 volumes Micronex in mercaptobenzothiazole stock
B—40 volumes Charlton in mercaptobenzothiazole stock

Figure 1—Effect of Aging upon Stress-Strain Curves

Modulus

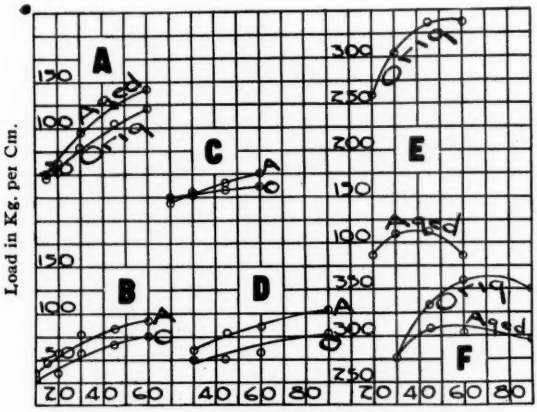
On aging the stress-strain curve becomes straighter. It usually tends to rise toward the stress axis, but the percentage increase in modulus is higher at the lower elongations. Sometimes the curve has an inflection point about midway and becomes concave toward the strain axis. These characteristics newly appearing or accentuated by aging may also be induced by excessive pigmentation and overcuring. Figure 1 gives two examples of the effect of aging upon the stress-strain curve.

In a few cases where diphenylguanidine was used and where the aging properties are poor, the modulus decreased. This decrease is greater at high elongations. The modulus *vs.* time-of-cure curve in most cases is steeper after aging than originally. In other words, the higher cures stiffen up more than the lower ones. This effect is shown in plots *A*, *B*, *C*, and *D* of Figure 2.

Tensile

The maximum tensile strength tends to appear at a shorter time of cure in the aged stock than in the original. This effect is shown for several stocks in Figure 2.

[5] **Park**, *Kautschuk*, **1926**, 57.



A—20 volumes Goodwin in hexamethylenetetramine stock
B—30 volumes Thermatomic in mercaptobenzothiazole stock
C—10 volumes Micronex in diphenylguanidine stock
D—30 volumes Charlton in ethylidene-aniline stock
E—10 volumes Micronex in diphenylguanidine stock
F—10 volumes Micronex in mercaptobenzothiazole stock
(All modulus results are at 500% elongation)

Figure 2—Effects of Aging upon Modulus Tensile

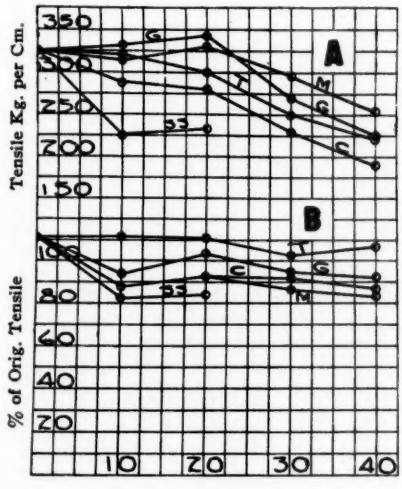
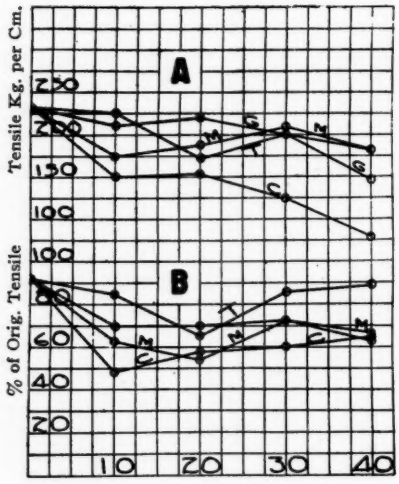
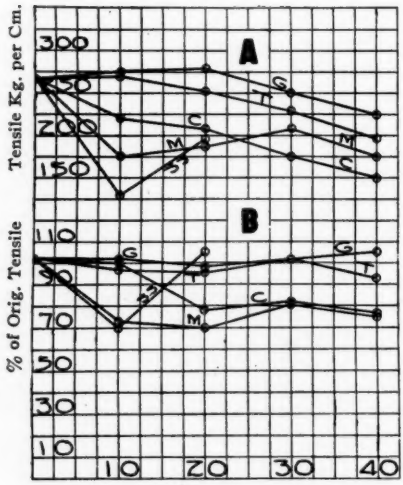


Figure 3—Mercaptobenzothiazole Stocks
Effect of Age on Tensile



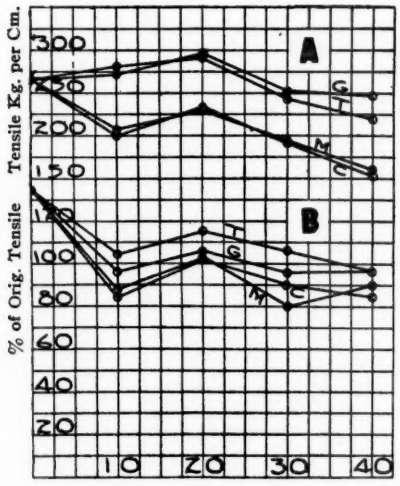
Volumes Black per 100 Volumes Rubber

Figure 4—Hexamethylenetetramine Stocks Effect of Age on Tensile



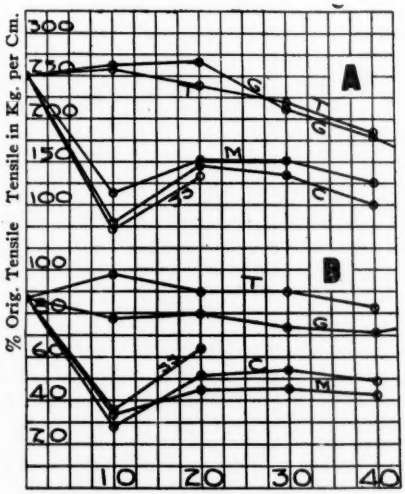
Volumes Black per 100 Volumes Rubber

Figure 5—Ethylidene-Aniline Stocks Effect of Age on Tensile



Volumes Black per 100 Volumes Rubber

Figure 6—Ethylidene-Aniline (Repeat) Stocks Effect of Age on Tensile



Volumes Black per 100 Volumes Rubber

Figure 7—Diphenylguanidine Stocks Effect of Age on Tensile

Figures 3 to 7, inclusive, show the effects of aging upon the tensile strength. In each figure plot *A* gives the relations between the optimum tensile of the aged stock and the volume loading. The optimum for each case was determined from data over a range of cures. In plot *B* the per cent of the original tensile is plotted against the volume loading. These two plots, therefore, give an accurate idea of the comparative aging behavior and also of the comparative properties of the stocks at the end of the aging period. The carbon black used in each case is designated on the curve by the first letter of the name.

In some cases, particularly the hexamethylenetetramine stock, the results leave much to be desired. However, casual inspection of the charts shows that Micronex, Super Spectra, and Charlton are decidedly inferior in aging behavior to Thermatomic and Goodwin. Thermotomic seems the best of the group and on the average Charlton seems slightly better than Micronex. Data on Super Spectra are so meager as to make its exact position doubtful.

The aging of mercaptobenzothiazole and ethylidene-aniline stocks is superior to that of hexamethylenetetramine and diphenylguanidine stocks. The latter have long been known to have poor aging properties. The final quality of the stocks indicates that mercaptobenzothiazole is superior to ethylidene-aniline.

Attention should be called to the difference in the two ethylidene-aniline stocks (Figures 5 and 6). The sulfur used in the first set of stocks was strongly acid. These tests were disregarded and a new set of stocks was prepared. Both stocks were kept in order to observe the effect of the acid upon aging. Inasmuch as there are no notable differences, this result may be regarded as substantiation of the statements of Wiegand[6] regarding the effect of zinc oxide in neutralizing acid sulfur.

The evidence concerning the effect of loading upon the aging is not convincing. There seems to be a slight tendency toward poorer aging properties with higher loadings, but the slope of the percentage curves is gentle enough to cast some doubt upon the validity of this conclusion.

Abrasion

Figures 8, 9, and 10 give the abrasion results. As certain changes were made in the bearings of the abrasion machine and the method of removing buffings, it has not been considered advisable to represent the effect of age in per cent of original results. Accordingly, the original optimum abrasions are shown in each figure on the left-hand side and the optimum abrasions of the aged stock on the right-hand side. In all cases volume loss is plotted against the volume loading of the stocks. Where the lines are dotted the point is based upon a single observation or there is some doubt as to the

[6] *Can. Chem. J.*, **4**, 160 (1920).

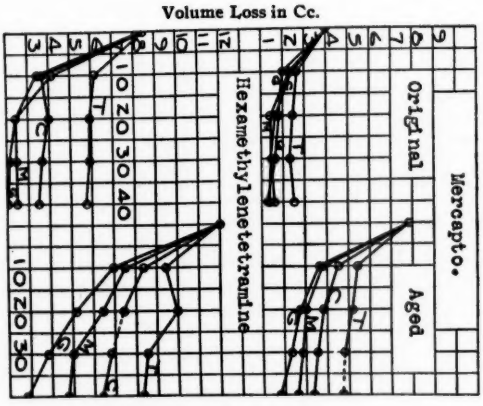


Figure 8—Abrasion

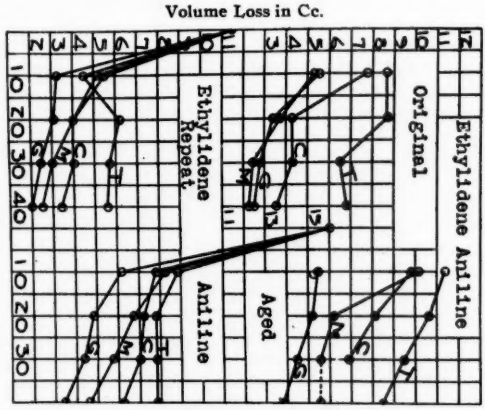


Figure 9—Abrasion

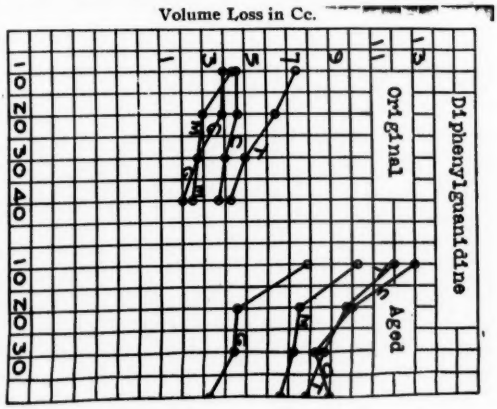
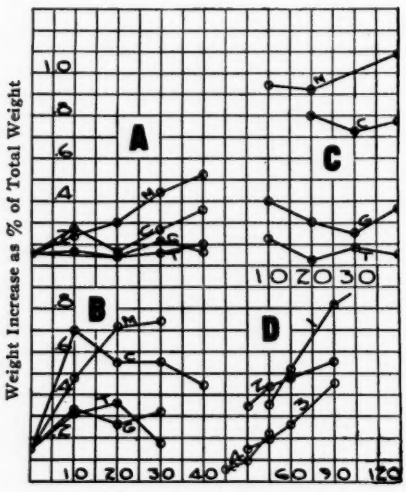


Figure 10—Abrasion

reliability of the data. In general, the results bear out the tensile tests in showing that Goodwin is better in its aging properties than Micronex. In most cases, Charlton is separated from Micronex to about the same extent in the aged stock as in the original. The separation between Thermatomic and Charlton is on the average somewhat decreased. Unfortunately, in spite of the superior aging properties of stocks containing Thermatomic black, it is not a desirable pigment from the standpoint of resistance to abrasion.

Weight Increases

The abrasion rings were carefully weighed before being placed in the aging cabinet and again after the aging period and previous to the test on the abrasion machine. The data



Volumes Black per 100 Volumes Rubber — Time of Cure in Minutes

Figure 11—Weight Increases Based on Total Weight

on ethylidene-aniline were not complete enough to justify plotting. The results on stocks cured with mercaptobenzothiazole, hexamethylenetetramine, and diphenylguanidine are shown in Figures 11 and 12, *A*, *B*, and *C*. In Figure 11 the per cent increase in weight is plotted against the volume loading at a given cure. The cure so plotted in the case of the mercaptobenzothiazole stocks was 45 minutes; that of the hexamethylenetetramine stocks was 60 minutes, and of the diphenylguanidine stocks 45 minutes for all except the Thermatomic, which is at 30 minutes. This method of plotting the data probably favors the Charlton and Micronex stocks, which were nearer the optimum cure than Thermatomic and Goodwin stocks.

In Figure 12 the same results are plotted as per cent of the weight of rubber in the compound. The weight increase is evidently dependent upon both the carbon black used and the accelerator.

The relations shown by this property are similar to those shown by the physical tests. The data that were available indicated that ethylidene-aniline stocks were similar to the mercaptobenzothiazole stocks in regard to weight increase. A single test on the stocks containing acid sulfur gave a result practically identical with the stock containing the good sulfur.

The weight increase depends upon the time of cure, as shown in Figure 11 (*D*). The curves labeled 1 and 3 are hexamethylenetetramine stocks, number 1 containing 20 volumes of

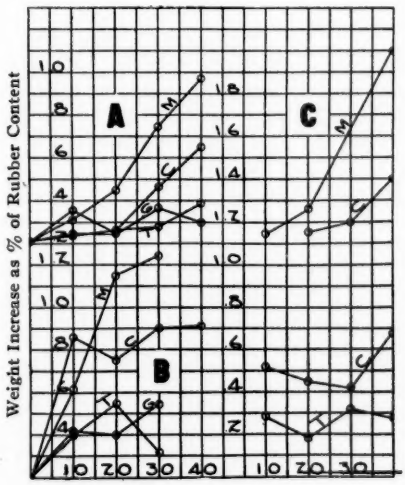


Figure 12—Weight Increases, Based on Rubber Content

Charlton and number 3 containing 40 volumes of Goodwin per 100 volumes of rubber. Curves labeled 2 and 4 are mercaptobenzothiazole stocks. Number 2 contains Micronex and number 4 Goodwin. Both are 30 volume stocks. A large amount of evidence has been presented by various investigators concerning the effect of oxygen during aging. In view of this information it seems safe to conclude that the weight increases here given represent the rates of oxidation of the various compounds. It is not surprising to find that in general the stocks which have aged badly physically show high oxygen absorption. In this connection it may be of interest to mention the result of some other experiments where weight changes were more closely followed. It was noticed that the increase in weight was preceded by a slight decrease. This decrease may be due to the formation of vol-

atile oxidation products which have been mentioned in various places in the literature.

The differences in aging behavior caused by the different carbon blacks seem to be closely connected with their adsorptive capacities. It is to be expected that those blacks with very active surfaces will carry larger quantities of oxygen into the stock and be more active in re-adsorbing and transferring further quantities to the rubber.

Effect of Stearic Acid

Fairly extensive tests have been made upon mercaptobenzothiazole stocks with and without stearic acid. The presence or absence of this ingredient seems not to affect the aging properties of the compounds. Differences in the stress-strain relations which were pointed out previously persist during the aging period.

Summary

1—The aging properties of compounded rubber stocks are affected by the carbon black which is used.

2—The order of increasing superiority for the blacks tried is Super Spectra, Micronex, Charlton, Goodwin, and Thermatomic.

3—The order of increasing superiority of accelerators is diphenylguanidine, hexamethylenetetramine, ethylidene-aniline, mercaptobenzothiazole. The last two are put in this order mainly because of the inferior original properties of ethylidene-aniline.

4—Results of tensile, abrasion, and weight increase tests are in reasonably good agreement.

5—The effect of acidity in any compounding material is neutralized in a stock containing zinc oxide.

6—Stearic acid is without effect upon aging properties of cured rubber.

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Carbon Black[1]

I—A Study of Its Volatile Constituents

C. R. Johnson

GODFREY L. CABOT, INC., BOSTON, MASS.

The rates of evolution of gas from carbon black with variation of time, temperature, and pressure have been determined.

Complete analyses have been made of five types of carbon black, which involve an organic combustion of the original sample, an organic combustion of the sample after the gases have been removed, a determination of the loss in weight represented by the gases removed, analyses of the gases removed, and finally a complete accounting, or balance, of the carbon in the steps considered. In an attempt to supply some missing information not revealed by the foregoing, some special gas analyses under varying conditions were made.

The relationship between the amount and composition of volatile matter evolved from carbon blacks and the properties imparted to vulcanized rubber when compounded with these blacks has been studied.

IT IS indeed surprising that there exists in the literature no complete chemical analysis of carbon black, when one considers the enormous importance of this material in several industrial fields. Were it not for the use of carbon black in the treads of automobile tires, the annual tire bill of the American motorists alone would be increased over five hundred million dollars. Without carbon black it would be impossible to manufacture a printing ink which could be

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

used on modern high-speed newspaper and job presses and have the necessary flow and covering power to be easily readable.

For a long time it was assumed that carbon black was practically pure carbon. This error was no doubt due to the fact that when burned in air or oxygen no ash was found. In 1912 Cabot[2] emphasized the fact that carbon black was not pure carbon; that carbon blacks showed on combustion from 85 to 95 per cent of carbon and the presence of hydrogen, oxygen, and nitrogen. Its ability to absorb moisture was already recognized.

The Bureau of Mines[3] presents the best available figures on the chemical composition of carbon blacks. The data for ultimate organic composition cover a wide range of blacks. Unfortunately, an ultimate organic analysis does not give a complete view of the components of a complex substance like carbon black, as it does not reveal the exact status of the carbon, hydrogen, and oxygen. The authors do reveal the amount of the volatile constituents given off when the samples are heated to 955° C., as determined by a Bureau of Mines method for coal analysis.[4]

The same bulletin[3] presents some work done in coöperation with G. A. Hulett and H. E. Cude, at Princeton University, on the adsorbed gases of carbon black. These investigators pumped the gases off at the desired temperature and analyzed them. They found that at room temperature the gas had the composition of air and a volume approximately that of the voids in the carbon black. At 445° C. a larger amount of gas was given off, which was chiefly carbon dioxide and carbon monoxide, together with appreciable percentages of nitrogen. No hydrogen was found at these temperatures. Not enough data were obtained to permit conclusions as to the relation of the adsorbed gases and the chemical and physical properties of carbon black. The amount of hydrogen revealed by the organic combustions in the Bureau of Mines bulletin calls for its appearance in some form in the gases or vapors evolved when carbon black is heated. In fact, this paper reveals that hydrogen is evolved provided the black is heated to sufficiently high temperatures.

In the findings of the work just considered, the authors assume that the gases which they found were adsorbed on the carbon black. There is considerable question as to whether this is correct. Here we have a substance which ultimate analysis shows to contain carbon in large percentage, together with oxygen, hydrogen, and nitrogen. What is the exact status of these last three elements in this material? Do they exist as adsorbed gases? Is the oxygen there as elementary adsorbed oxygen, or is it present in the form conceived by Langmuir[5] in his work with the carbon filament lamp con-

[2] *Orig. Com. 8th Intern. Congr. Applied Chem.*, **12**, 13 (1912).
[3] Bur. Mines, *Bull.* **192**.
[4] Bur. Mines, *Tech. Paper* **8** (1913).
[5] *J. Am. Chem. Soc.*, **37**, 1154 (1915).

taining oxygen in varying quantities—to wit, in quasichemical union at the surface? Is there an excess amount of oxygen there beyond the requirements of the Langmuir concept? Is there any carbon monoxide or carbon dioxide present as adsorbed gas? Or are these gases simply the product of reactions taking place when the carbon black is heated? Is the hydrogen there as elemental gas adsorbed as such or is it in definite chemical combination with the carbon? These questions only emphasize the fact that our knowledge of the composition of carbon black is far from complete. When one considers the situation when carbon black is manufactured, these possibilities do not seem at all fantastic. A mixture of methane, ethane, and small quantities of higher hydrocarbons is subjected to incomplete combustion. According to the latest concepts of the mechanism of the combustion of gases, carbon can be formed by the cracking of the ethane or methane or as the result of partial combustion. At any rate, we can assume that just at the moment of formation of the black we have present oxygen, carbon dioxide, carbon monoxide, hydrogen, nitrogen, and even unburned natural gas.

It was because of the discovery, by the author, of important relationships between the amount of volatile matter contained in carbon black and the reënforcing properties of this material when vulcanized with rubber that a study of the nature of these volatile constituents was undertaken. The correlation of a large number of rubber tests using carbon black as a reënforcing pigment with the amount of volatile matter contained in the carbon blacks showed that the amount of volatile matter was variable and that when it varied beyond certain limits, the carbon black was deficient as a reënforcing agent and retarded the rate of vulcanization.

Carbon Blacks Used

Sample A. A carbon black produced by the channel process in Texas using 20-foot tips and of a quality used in rubber. This black shows good physical testing values in rubber.

Sample B. From the same factory as sample A and produced under presumably the same conditions, but showing poor physical tests when vulcanized with rubber.

Sample C. A carbon black produced in Louisiana by the channel process using 10-foot tips and designed for use in rubber. This black also shows good results when vulcanized with rubber.

Sample D. A carbon black produced by the roller process and designed for the ink trade. It is known as a "long" black in contrast with the short blacks which are used in the rubber trade.

Sample E. Another carbon black produced by the roller process and differing in ink working properties from D. This black is also a long black.

Note—The property of length produced in printing inks by the use of "long" black is difficult to describe, as there is no standard test by which it is determined and ink makers have different ways of judging it. One of the usual ways of judging length is to grind the black in a standard ink varnish and then pick up some of the ink on a spatula. If the ink runs off the spatula in a long, thin string, the black has good length. A short black mixed with the same varnish will not develop a string, but breaks off quickly.

Determination of Volatile Matter of Black under Varying Conditions

The standard method for determining the volatile matter was to heat about 1 gram of the sample for 7 minutes at 955° C. in a quartz or platinum crucible fitted with a capsule cover to exclude air. The loss in weight minus the amount of moisture in the sample was taken as the amount of volatile matter and reported as a percentage of the original sample. A Hoskins electric furnace of the Fieldner type was used. Moisture was determined by heating the sample in an oven at 105° C.

The volatile matter contained in the five samples of carbon black examined is shown in Table I.

Table I—Volatile Matter Content of Carbon Blacks

Sample	Volatile Matter
	Per cent
A	4.49
B	6.67
C	4.00
D	8.44
E	12.63

For the purpose of determining the characteristics of volatile matter evolution, a series of determinations was made on sample A in which time, temperature, and pressure were varied.

Effect of Temperature—The results of the determination where the temperature was varied and the sample was heated for 7 minutes are shown in Figure 1 and Table II.

Table II—Effect of Temperature on Evolution of Volatile Matter

Temperature	Volatile Matter	Temperature	Volatile Matter	Temperature	Volatile Matter
° *C.*	*Per cent by weight*	° *C.*	*Per cent by weight*	° *C.*	*Per cent by weight*
200	None	455	0.15	677	1.99
300	None	480	0.28	870	3.67
400	None	538	0.57	955	4.56

At 955° C. no change of slope is evident and it is regrettable that the upper limit of temperature of the furnace was reached before the complete characteristics of the curve were determined. From a consideration of the data in Figure 2, in which time was varied, it might be expected that the slope of the curve above 955° C. would fall off quickly to a slight positive slope.

Effect of Time of Heating—Sample A was next heated by the regular method except that the time was varied. The data are plotted in Figure 2. It will be seen that the bulk of the gas is evolved in the first 5 minutes, when the curve flattens considerably. From 10 to 20 minutes there is an increase in rate. From some data reported later in connection with the gas analyses, it might be considered that this increase is due to the evolution of hydrogen contained in the black which does not come over so readily as the carbon monoxide and dioxide. The curve finally assumes a

fixed slope, which undoubtedly represents for the most part the combustion of carbon due to the slow diffusion of air into the crucible.

VARIATION IN TEMPERATURE AND PRESSURE—For the determination of the rates of evolution of gas with variation of temperature and pressure a quartz test tube fitted with a

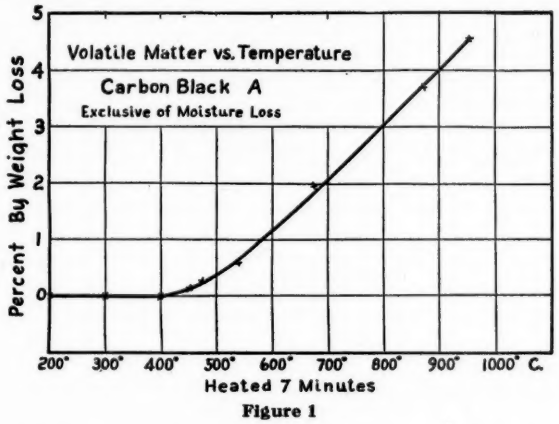

Figure 1

ground-glass stopper was used instead of the platinum crucible for heating the sample. This test tube was connected to the vacuum source and a mercury manometer. The sample of black was placed directly in the test tube. The first series of runs was made varying the temperature at two pres-

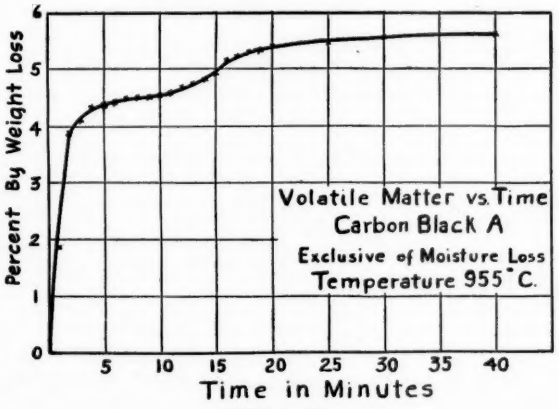

Figure 2

sures, atmospheric and 2 mm. of mercury. The results (Figure 3) show lower volatile matter loss at low pressure for all temperatures, probably because the gases are released faster from immediate contact with the carbon and consequently less carbon is burned in the determination.

EFFECT OF PRESSURE—The amount of volatile matter

in sample A when heated for 7 minutes at 955° C. at varying pressures is plotted with logarithmic abscissas for pressures in Figure 4.

Apparently, once the volatile matter has been driven off from carbon black at 955° C., the black no longer has the property of adsorbing gas to a large extent. The residue from a determination of volatile matter on sample A was exposed to the atmosphere for 24 hours and then the volatile matter was redetermined. The amount was 0.65 per cent. Another sample was treated in the same way except that it was slowly cooled in the furnace to 482° C. and then exposed for 24 hours. The value in this case was 1.16 per cent. The same results occur with respect to moisture. Once the sample has been heated to 955° C. for 7 or more minutes, it no longer possesses the hygroscopic property so characteristic of carbon black. A sample of black heated for 7 minutes at 955° C. and exposed to the atmosphere for 24 hours took

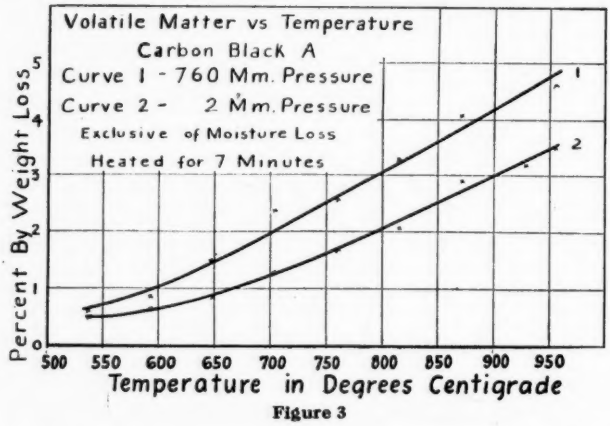

Figure 3

on 0.24 per cent moisture, whereas normally the black would contain from 1.5 to 2.5 per cent. A sample of carbon black A was heated for about 30 minutes at 955° C. The moisture of the residue was determined as soon as cool and found to be 0.13 per cent. After exposure to the atmosphere for 48 hours, it was 0.17 per cent.

Analysis of Carbon Black

In order to throw more light on the real composition of carbon blacks, an attempt was made to gather more complete data than have been published before. The scheme which was followed was to make an ultimate analysis by organic combustion on the sample including its moisture content. For purposes of calculation the moisture was also determined. Following this, another portion of the same sample was heated for approximately half an hour at 955° C. and the gas evolved was collected and analyzed. An organic

combustion was then made on the residue from the heating. This combination of data permits the calculation of a carbon balance which serves as a check on the accuracy of the several determinations.

The procedure for obtaining the gas samples was to place the sample of carbon black in a quartz test tube fitted with a ground-glass stopper. Connected to the tube was a mercury manometer and a delivery tube to the gas holder. The system was exhausted to 1 mm. pressure to remove the air in the interstices of the black. The test tube was then placed in the furnace and as soon as the gas pressure was up to atmospheric, delivery was made to the gas holder containing a saturated solution of zinc sulfate. The apparatus used for the gas analysis was the Burrell-Oberfell type, which determines the hydrogen and carbon monoxide by combustion with copper oxide. The ethane and methane were determined with a slow-combustion pipet. The results reported are from check analyses and are reliable in respect to all gases, except possibly the methane and ethane. The amount of the residual gas after the copper oxide combustion was so small that it was difficult to get concordant results on these two gases. This method requires the assumption that the remaining combustible gases are either methane or ethane, and it is doubtful if any of the higher homologs of the methane survive the combustion reaction in the manufacture of carbon black in sufficient quantity to affect the accuracy of this assumption.

In view of the small amounts of nitrogen and sulfur reported by the Bureau of Mines,[3] and the general confirmation in the amount of nitrogen found in these gas analyses, it was not considered important to make organic nitrogen and sulfur determinations. Accordingly, since the oxygen of the combustions is determined by difference, the values are high by approximately 0.2 to 0.4 per cent.

The data for these analyses are given in Table III. The analyses of the gases from samples A, B, and C show practical uniformity among these three carbon blacks. Sample B differs from A and C especially in the amount of the volatile matter given off and in the oxygen in the original sample. The significance of this will be discussed later in connection with the rubber test with the blacks. Samples D and E are not rubber blacks, but belong to the class known as "long" blacks. The outstanding characteristics of these two blacks are the high volatile matter content and the high original oxygen content. These two blacks show considerable differences in respect to hydrogen and carbon dioxide. It will be noticed that in all cases the hydrogen is not greatly reduced by heating to 955° C. after making allowance for the hydrogen contained in the moisture of the sample. This points very strongly to the conclusion that the hydrogen is not there as an adsorbed gas, but is in definite combination with the carbon as a hydrocarbon.

Table III—Analytical Data on Carbon Blacks

Constituent	Sample A	Sample B	Sample C	Sample D	Sample E
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
As received:					
Carbon	95.00	92.30	95.30	90.75	87.50
Hydrogen	0.85	0.97	0.81	0.91	0.95
Oxygen	4.15	6.73	3.89	8.34	11.55
After heating:					
Carbon	98.90	98.30	98.90	99.10	98.20
Hydrogen	0.37	0.55	0.57	0.52	0.70
Oxygen	0.73	1.15	0.53	0.38	1.10
Loss on heating	6.14	9.68	6.02	12.63	17.43
Moisture	1.35	2.71	1.73	2.92	4.32
Volatile matter	4.79	6.97	4.69	9.71	13.11
Water of combination[a]	0.30	0.44	0.45	0.44	0.72
Per cent weight in gases analyzed[b]	4.49	6.53	4.24	9.27	12.39

GAS ANALYSIS

	% vol.	*% wt.*	*% vol.*	*% wt.*	*% vol.*	*% wt.*	*% vol.*	*% wt.*	*% vol.*	*% wt.*
Carbon dioxide	14.53	1.178	14.65	1.735	14.40	1.056	18.68	3.161	27.18	4.860
Illuminants	0.16	0.030	0.38	0.101	0.17	0.028			0.17	0.069
Oxygen	1.15	0.071	1.36	0.117	0.83	0.044	0.74	0.092	0.76	0.099
Hydrogen	22.72	0.084	24.85	0.133	23.37	0.078	26.15	0.200	7.57	0.061
Carbon monoxide	54.45	2.805	52.40	3.930	56.18	2.810	51.35	5.530	60.60	6.890
Ethane	0.04	0.002			0.11	0.005	0.04	0.004	0.08	0.010
Methane	1.62	0.048	1.19	0.052	0.72	0.019	1.31	0.080	0.72	0.047
Nitrogen	5.33	0.275	5.97	0.448	4.22	0.197	1.74	0.188	2.92	0.332

[a] Determined by heating sample at 955° C. in quartz combustion tube, flushing with nitrogen, and determining moisture absorbed in calcium chloride tube. The water of combination is taken as the total water absorbed in the calcium chloride less moisture found in sample by heating for 1 hour at 105° C.

[b] Calculated from percentage by volume using as base volatile-matter loss corrected for water of combination.

CARBON BALANCE—To illustrate the carbon balance in the scheme of analysis which was used, the following computation is given for sample B:

	Per cent	*Per cent*
Carbon in original sample	92.30	
Less C in CO_2 found in gas		0.472
Less C in CO found in gas		1.682
Less C in CH_4 found in gas		0.039
Total loss carbon		2.193
Balance carbon	90.11	
Carbon found in residue by combustion		98.3
Corrected to original sample weight	90.06	

OXYGEN STATUS—The analytical data does not fully answer the questions asked at the beginning of the paper concerning the status of the oxygen as revealed by the ultimate analysis. Under the temperature conditions of the reaction it is possible for the oxygen, if present as such, to combine with the carbon to form carbon monoxide and carbon dioxide, as well as with the hydrogen. In order to throw more light on this phase of the question, two additional observations are given.

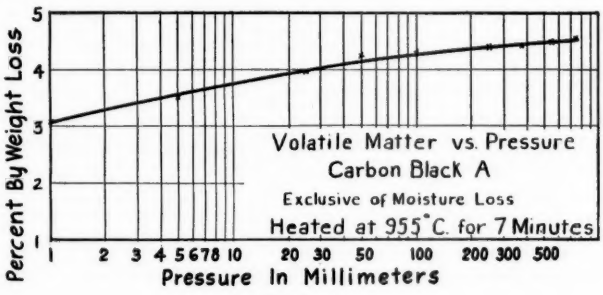

Figure 4

The first experiment was to subject a sample of carbon black A to a temperature of 955° C. under a very low pressure for approximately half an hour, and analyze the gas evolved. The apparatus consisted of the usual quartz test tube connected to a Cenco Hyvac pump, a McLeod gage, and a Töpler mercury pump. The primary vacuum was obtained with the Hyvac and as soon as the best vacuum was reached the test tube was placed in the electric furnace, the primary pump shut off, and the vacuum maintained with the Töpler pump, which at the same time compressed the sample and delivered it to a reservoir available for analysis. The pressure at the start of the heating was 0.048 mm. mercury. During the heating when the gas evolution was most rapid, the pressure in the system increased to 17 mm. In Table IV the analysis of the gas is given both at the original and at atmospheric pressure.

The increase in oxygen, though slight, and the decrease in carbon dioxide and carbon monoxide in the sample taken at low pressure are significant and confirm the idea that these gases are reaction products.

Table IV—Gas Evolved from Carbon Black A at Two Pressures

	Low Pressure	Atmospheric Pressure
	Per cent by volume	*Per cent by volume*
CO_2	7.42	15.17
Illuminants	0.32	0.16
O_2	1.36	0.91
H_2	37.05	23.27
CO	46.35	53.25
C_2H_6	...	...
CH_4	0.88	1.545
N_2	6.62	5.70

Another evidence that the oxygen of carbon black is present in elemental form is the fact that all the volatile matter determinations made at low pressure were smaller than when run at atmospheric pressure. (Figure 3) The explanation which is offered for this difference is that the gases are withdrawn more rapidly under low pressure and the opportunity for the oxygen to unite with the carbon is reduced.

Langmuir's conclusion that the surface of the carbon filament of an electric lamp is covered with oxygen atoms in stable combination with the carbon can no doubt be applied to carbon black, for there is little reason to believe that the property which he found in the carbon filament is different in carbon black. The extremely finely divided state of carbon black provides an enormous surface for this phenomenon. The weakness in this reasoning is the assumption that carbon black behaves toward oxygen the same as a carbon filament.

Comparative Rate of Gas Evolution—To determine whether the gases come off from heated carbon black in uniform composition during the entire period of evolution, the gas from one heating of sample A was divided into two portions. The first portion was that which came over during the first 3 minutes; the second portion came over during the following 27 minutes, and had about four times the volume of the first. The analyses of these two samples of gas are given in Table V.

Table V—Composition of Gas at Various Stages of Evolution

Gas	First Portion	Second Portion
	Per cent	*Per cent*
CO_2	17.38	9.26
Illuminants	0.15	0.14
O_2	2.01	0.43
H_2	10.70	30.50
CO	58.30	55.85
C_2H_6	...	0.19
CH_4	1.49	0.84
N_2	9.97	2.79

This experiment proves that the hydrogen comes off with greater difficulty.

Relation between Amount and Composition of Volatile Matter of Blacks and Properties Imparted to Vulcanized Rubber

Comparison of a large number of volatile-matter determinations of carbon black with the physical rubber tests, revealed a very definite relationship, which may be stated as follows: Whenever the volatile matter of a rubber black

rises above a particular limit for that black, its reënforcing properties in rubber compounds suffer and the cure is retarded. This value can be fixed for any black from any factory but varies slightly for every black. Table VI gives the volatile matter of a number of samples from the same factory compared with their physical tests. The first three

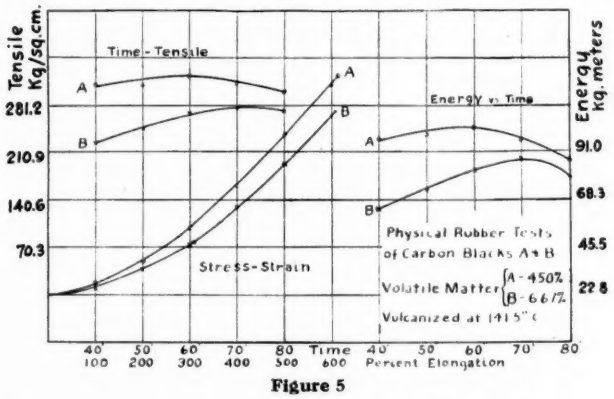

Figure 5

samples have a low volatile content and test well. The next two are border-line cases with moderately high volatile and fair rubber tests. The last three are high volatile and show poor tests.

Table VI—Relation between Volatile-Matter Content of Blacks and Physical Properties of Rubber

Sample	Volatile Matter	Tensile at Break			Modulus at 400%		
		40 min.	60 min.	80 min.	40 min.	60 min.	80 min.
	% by wt.	*Kg. per sq. cm.*			*Kg. per sq. cm.*		
143	5.10	290	305	306	118	148	161
145	4.91	296	311	310	119	141	155
163	4.60	305	317	306	122	149	158
112	5.60	256	288	290	99	123	139
157	5.73	264	297	302	109	139	153
91	6.19	236	266	272	89	109	109
16	6.67	225	273	268	103	128	142
308	7.56	128	155	160	66	85	96

The samples of black were mixed by the following formula, which is designed to bring out differences of carbon black when vulcanized with rubber. In some regular tread compounds these differences are not so pronounced.

	Parts
Smoked sheets	93.0
Carbon black	35.0
Zinc oxide	3.0
Sulfur	5.0
Diphenylguanidine	0.75
	136.75

The mix was aged 24 hours, vulcanized at 141.5° C., and tested after 24 hours' aging.

The differences in quality imparted to vulcanized rubber are further illustrated in Figure 5, in which the characteristics of samples A and B are shown. The higher volatile-

matter content is clearly reflected in the poorer quality of all the tests.

The physical tests of rubber compounds containing each of the five samples considered in this paper are given in Table VII. The same mixing formula is used in each case.

Table VII—Rubber Tests of Carbon Black Samples

Sample	Time of Cure at 141.5° C.	Tensile at Break	Elongation at Break	Tensile at 400% Elongation	Hardness
	Minutes	*Kg. per sq. cm.*	*Per cent*	*Kg. per sq. cm.*	
A	40	310	630	141	65
	60	324	613	163	68
	80	301	555	178	70
B	40	225	602	103	60
	60	273	612	128	63
	80	268	580	142	66
C	40	300	675	118	61
	60	308	610	148	65
	80	303	603	161	69
D	40	167	610	65	52
	60	186	580	82	56
	80	193	570	92	59
E[a]	40	238	610	81	60
	60	264	603	101	63
	80	257	598	110	65

[a] Four times as much diphenylguanidine was used with this sample.

The long blacks of high volatile content show very poorly in these tests. In the case of sample E it was not possible to get sheets for test with the regular formula at the usual time of vulcanization because of extreme undercure. Accordingly, a mixture was made using four times the amount of diphenylguanidine as the accelerator. Evidently in the case of high-volatile blacks some side reaction with the accelerator occurs which so diminishes its concentration that there is no longer enough to accelerate the vulcanization reaction properly.

Some technologists who have specialized on the problems in connection with solid tires for motor trucks have expressed the opinion that the cause of blowouts in solid tires is the evolution of gas from the carbon black. The results as given in Figure 1 are contrary to this conclusion, because no gases are evolved in carbon black until a temperature considerably above that occurring in solid tires when run under heavy load and high speed. It can be fairly safely concluded that the gas which comes from solid-tire blowouts is from the breakdown of the rubber hydrocarbon from the heat generated in the tire, instead of the gas from carbon black.

Several instances of the difficulty encountered in the mixing of some lots of carbon black with rubber, especially in internal type mixers, have recently been called to the writer's attention. The temperature of the mix rises so high that the process has to be stopped. One instance has been given when this took place on an open mill. Two samples exhibiting this condition have been examined and found to be abnormally low in volatile matter. Might it not be possible that the gas contained in carbon black acts as a lubricant to assist dispersion into the rubber and when the black is deficient in gas, an excessive amount of heat is generated in the mixing by the lack of lubrication?

Acknowledgment

Acknowledgment is due to R. K. Estelow and Jacob Gabry, who did a large share of the experimental work in connection with this investigation.

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Softeners and Anti-softeners[1]

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In the manufacture of rubber goods various materials are incorporated with the rubber in order to produce a mixture that will process more easily. Such materials are usually called fluxes or softeners.

A simple method of determining the relative effects of such materials is described. This consists in mixing the material in rubber under standardized conditions and determining the plasticity of the product by the Williams method.

Some materials show stiffening instead of softening action and both types are shown in the results reported in this paper. Benzidine and *p*-amidophenol are examples of materials which stiffen rubber.

MANY materials used in the compounding of rubber exert an influence on the plasticity. Usually a material is specifically added to increase the plasticity and is called a softener, but in some cases the effect on plasticity is purely incidental to some more important function, such as acceleration or protection against deterioration on aging. The effect of this class of materials may be towards either a more or a less plastic mix; in the latter case it is correct to class the material as an antisoftener.

Softeners or fluxes may be divided into two classes according to their action—true softeners and lubricants. The work described in this paper is confined to the evaluation of those materials which definitely affect plasticity of the

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

rubber. In other words, no consideration is given to materials which affect the workability of raw-rubber mixtures chiefly through a lubrication or dispersing action on the pigments—i. e., substances which act through their influence on the interfacial tension, or affect the wettability of the pigment.

No attempt has been made to study shrinkage, which, although an important item in the processing of a rubber mixture, may be eliminated by correctly using materials which produce the proper plasticity. If true softening is obtained the shrinkage is reduced, but if the reverse action, antisoftening, occurs, shrinkage may become pronounced. Shrinkage also results when set-up or premature vulcanization takes place and is always caused by the generation of too much heat in processing stiff stock.

Determination of Softening Effects of Various Materials

Much has been written on various rubber softeners, but there is little available which gives a numerical evaluation. Two instruments have been developed for the measurement of crude rubber plasticity—the Marzetti extrusion apparatus[2] and the Williams press.[3] Both types have been modified by several investigators and Burbridge[4] in his work used a modification of the Williams press.

The work of Burbridge is an outstanding contribution and his method can be briefly summarized as follows: A batch of standard stock is milled for 25 minutes. The formula for this batch is: massed pale crepe 100, zinc oxide 1, sulfur 5, and diphenylguanidine 0.25 parts. Into this master batch various percentages of several substances are incorporated by milling. Plasticity figures are obtained on the crude rubber, the massed rubber, and the finished batch. In determining the softening action a comparison is made of the finished batches with and without softener.

Several objections may be raised to this method:

1—The test as outlined requires a break-down of the master batch and no check is made on the amount of work actually done on it before the softener is added. This is a serious fault, for in breakdown the change in plasticity is very rapid.

2—A master batch containing curing ingredients is used as a standard and is subject to change in storage and during the actual test.

3—The master batch contains diphenylguanidine, which is a softener itself—a fact which this investigator did not observe.

4—The addition of an acid softener to a stock containing zinc oxide gives the effect of the zinc salt, not the actual softener.

The method described in this paper has been in use by the writers for several years and has none of these objectionable features.

As it is necessary to have a standard grade of rubber for use in all experiments, each batch is made up of pieces of

[2] *Giorn. chim. ind. applicata*, **5**, 342 (1923).
[3] IND. ENG. CHEM., **16**, 362 (1924).
[4] *Trans. Inst. Rubber Ind.*, **1**, 429 (1926).

rubber cut from various sheets from different bales. It should be noted that the blend is not massed. No single piece should exceed 100 grams in weight. Six hundred grams of rubber will process easily on a 30-cm. (12-inch) mill with 15-cm. (6-inch) rolls and as a 30-gram sample is removed for crude rubber plasticity during the test, the initial amount of rubber used is 630 grams.

Of equal importance is the initial temperature of the mill rolls. By experiment 60° C. has been found to be the most satisfactory, as a higher temperature gives too hot a batch to work with and a lower temperature makes the test unnecessarily long. This initial temperature should always be obtained by heating a cool mill up to temperature by milling rubber. The temperature of 60° C. can be measured by the use of a thermocouple pad and potentiometer but may also be gaged by feel after the operator has become proficient. After this initial temperature is obtained, it is made certain that both steam and water are shut off so that the temperature of the mill may rise as it will.

The third necessary standard is the method of milling. In this work a mill with 10:9 ratio and front roll speed of 30 revolutions is used and the time periods given in Table I may not hold true for all mills, but the procedure may be adapted to any mill with a little allowance for the new speed.

Table I—Milling Cycle

Time Elapse from Start		
Minutes	*Seconds*	
0	0	Crepe rubber through once
0	15	Open mill to 3 mm. (1/8 inch) and start massing
3	30	Cut rubber back and forth four times
5	0	Remove sample *A*
5	10	Start adding material to be tested
7	40	Cut mix back and forth four times
9	0	Remove from the mill

The first creping operation insures the rubber massing continuously and not lodging in a ball on top of the rolls. The time of knitting together should be between 2 minutes 45 seconds and 3 minutes and is a definite check on all variables up to this point. Sample *A* is obtained by removing a strip, weighing out 30 grams, and returning the excess to the mill immediately. Five per cent of softener is about the maximum amount used commercially so this percentage was adopted as the standard. Sample *B* is cut from the finished batch and may be any convenient size.

As these batches contain neither sulfur nor accelerator, it is permissible to obtain a plasticity figure as though the batch were crude rubber. The machine used is the one designed by Williams,[3] and *Y* value after 5 minutes in the press is obtained on samples *A* and *B*. The ratio of difference of the *Y* values of *A* and *B* to the *Y* value of *A* is the total softening percentage and is due to two causes—(1) the effect of the additional 4 minutes of milling, and (2) the effect of the ingredient added to the rubber. The total softening effect, minus the percentage drop due to milling as obtained by a

control run in which no softener is used, is the effective softening action of the ingredients added.

For example, the Y value of A of the control is 296, and of B is 256. Thus the percentage drop due to milling is 40 divided by 296 or 13.5 per cent. The Y value of the A sample before addition of hardwood pitch is 295 and of the B sample is 239, a drop of 56 points, or 19 per cent, which gives an effective softening action due to hardwood pitch of 19 minus 13.5, or 5.5 per cent.

Table II—Softening Action Expressed in Percentage Change in Plasticity

	Per cent		*Per cent*
Stearic acid	22	Perilla oil	11
Pine tar	16.5	Vaseline	9
Liquid asphalt	16.5	Mineral rubber	8
Pine oil	16	Straw paraffin oil	8
Degras	16	Cottonseed oil	8
Rosin oil	13	Hardwood pitch	5.5
Stearin pitch	11	Carnauba wax	5

Softeners

In Table II are listed a few of the better known softeners. It may be noted that pine oil and pine tar are similar in softening action, which probably explains why various viscosities of pine tar are about alike in their effect on plasticity. Also stearic acid by its superior power justifies a premium in price due to this property alone.

Burbridge[4] stated that carnauba wax is a stiffener and that it is hard to incorporate, but it has been found to be a softener similar to hardwood pitch. Perhaps the previous investigator did not consider the fact that in raising the initial temperature of the mill he greatly reduced the amount of breakdown.

Antisofteners

When the total percentage drop of any batch is less than the percentage drop of the control, it is evident that the substance added is a stiffener.

It is a well-known fact that some antioxidants exert softening action to such an extent that tubed articles lose their shape due to their weight alone. Several ways are open to overcome this and one of them is to use an antisoftener in the compound.

Benzidine, an antioxidant, accelerator-activator, and a fair stiffener of cured stock, is a stiffener of uncured stock of high degree, as evidenced by Table III.

Table III—Antisoftening Action of Benzidine

Benzidine to Rubber	Actual Stiffening	True Stiffening
Per cent	*Per cent*	*Per cent*
0.0625	21.9	35.4
0.125	31.9	45.4
0.25	26.7	40.2
0.5	22.7	36.2
1.0	2.5	16
2.0	2.5	16

Another material which behaves in a manner similar to benzidine is *p*-amidophenol, which gives its optimum stiffening action (43 per cent) when 0.5 per cent on the rubber is used. Other stiffeners which have been noted are β-phenylenediamine, β-naphthylamine, α-naphthylamine, tolidine, quinone, and dianisidine.

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Machine for Testing Rubber Products Used to Absorb Vibration[1]

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A machine for studying the effect of flexing rubber under compression is described. The operation of this machine in the testing of shock insulators, motor supports, and other rubber parts that absorb vibration, or undergo flexure under compression, is given in detail. Ordinary tests such as tensile and elongation are insufficient in evaluating such products. Furthermore, the more recent static compression-set test is not satisfactory. Results of tests on various stocks as given with this device check with dynamometer and service tests.

Under the conditions of test adopted the permanent set is shown to approach a maximum in 3 or 4 hours. The temperature of the test piece rapidly reaches a maximum value.

Data and curves are presented for comparison of set under flexure with tests under tension and with static compression.

WITHIN the last two years numerous rubber parts, other than tires and tubes, have become widely adopted in the assembly of automobiles. Virtually all of these new rubber parts are used to absorb vibration in one way or another. Nevertheless, no universally accepted

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

laboratory tests, of significance as far as actual service conditions are concerned, have been developed.

The quality and type of rubber products for such service have generally been determined from tensile, modulus, elongation, permanent set, and hardness data. It can easily be shown that such tests not only are inadequate but may be very misleading. Furthermore, most of them cannot be made on the finished product. Although a stock possessing high tensile strength may be considered as of better quality than one possessing low tensile, in the case of rubber products used to absorb vibration there certainly is a value above which increase in tensile does not mean better quality. This is, of course, true of many other products also.

Degree of cure has a decided effect on the degree to which vulcanized rubber withstands various service conditions. Nevertheless, many properties, particularly hardness, show no decided change with relatively large variations in cure. ("Hardness" of a rubber product may be defined as the resistance which the surface layers of this product offer to indentation by a penetrating element under a predetermined load.)

It is also to be noted that motor supports, rubber spring shackles, torque insulators, balls for universal joints, and similar parts, undergo permanent set due, to a greater or less degree, to flexure under compression.

Note—In this paper any force applied toward the interior of the rubber sample will be called a "compressive load." The deflection produced by such a force will, for the sake of simplicity, be called "compression" or "compressibility." In the work on materials used to absorb vibration we are probably little concerned at present, at least, with the true compressibility of vulcanized rubber, since this is so small as to be negligible.

Although there have been static compression tests for permanent set under a definite load and also under a definite distortion, there is a lack of uniformity in procedure and in results. It is shown later in this paper that one of the most common of these tests fails to evaluate such products, and, as far as the writer is aware, no satisfactory dynamic tests have been described in the literature. Mention is made of a repeated compression test in an unsigned article,[2] but neither data nor comments are given. None of the above tests simulate service conditions to any extent.

Because of these unsatisfactory conditions a new machine, called a compression flexometer, was designed, which tests the resistance of vulcanized rubber to flexure under compression.

Description of Flexometer

The compression flexometer (Figure 1) consists of a fixed bottom plate with rocker bolts hinged to it which pass through a top plate, which is attached to a driving device. By screwing nuts down on these rocker bolts the top plate may be

[2] *Rubber Age*, **20**, 601 (1927).

made to produce a compressive load on a test piece placed between the two plates. The top plate is made to oscillate at 800 cycles per minute. The oscillations are secured by setting the thrust arms off center with respect to the drive shaft. It is possible to increase the range of oscillatory movement (throw) to over 10 cm. (4 inches) over-all by means of the slots cut in the eccentric collar shown at *A*. Tests recorded in this paper were made with a 0.95 cm. ($^3/_8$-inch) over-all throw. The compressive load is produced by the weight of the top plate and a component part of the thrust arms (a total of 13.6 kg. or 30 lbs.) plus that secured by tightening the nuts shown on the top plate. A standard load is chosen for a given size of test piece. The tests herein reported were run at constant distor-

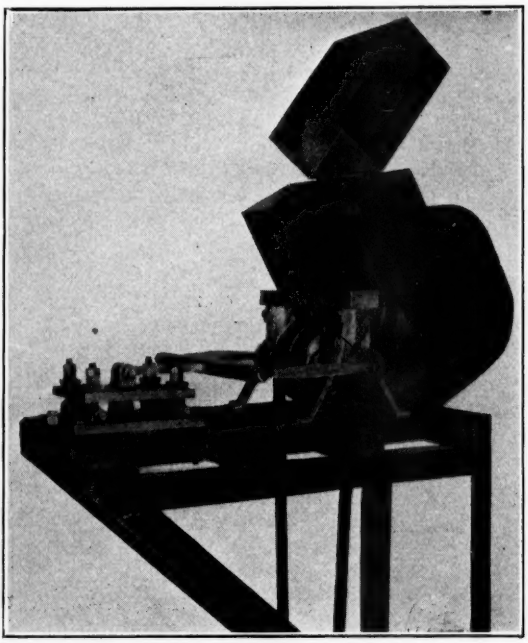


Figure 1—Compression Flexometer

tion. For a purely technical study of rubber stocks, involving the effect of pigments and other ingredients, tests can also be made under a constant load by means of lead weights fastened to the top plate. This work will be reported in a future paper.

The duration of the tests under various conditions, although arbitrarily chosen, is such that the permanent set developed in various high-quality stocks is great enough to insure a low percentage error. Tests on materials to absorb vibration are stopped far short of complete physical breakdown or blow-out, which is, in general, an explosive

rupture of the test piece due to gaseous and liquid products produced by the heat of flexure.

Method of Making Test and Calculation of Results

The test piece, which has been molded, or cut and buffed, to the desired shape and size, is carefully centered on the bottom plate of the compression flexometer. Care is taken that flexure and loading occur in the same respective directions as in service. The top is then carefully lowered onto the sample while the machine is at dead center. The desired compression (uniformly secured) is obtained by means of the nuts on the top plate. The flexing is then started. Ordinarily the sample is removed from the flexometer immediately at the conclusion of the flexure and allowed to cool 1 hour. The test piece is then bisected in a vertical plane in the direction of flexure. The least height of this cross section in the direction of the loading is measured. The loss in height is reported as per cent flexure-set.

With stocks of the pure-gum type virtually no set is developed under the ordinary conditions of test. In order to produce flexure-set in such stocks the severity of the test must be increased. This may be done by increasing the pressure, increasing the duration of the flexure, increasing the amplitude of flexure, or, by allowing the test piece to stand under load in the machine at the completion of the flexing. If the last method is adopted the machine should be stopped at dead center. A combination of and of these four methods is, of course, possible.

Table I—Accuracy

Stock	Flexure-Set		Time of Flexure	Deflection
	Sample 1	Sample 2	*Hours*	*Per cent*
8	36.0	36.0	2	55.5
3	34.4	34.4	2	50
30	29.5	31.2	2	50
1	43.1	41.7	2	50

In all tests reported in this paper the samples rested on a block of oak 3.81 cm. ($1^1/_2$ inches) high. This resulted in a higher temperature (82° C. in stock No. 1, Figure 6) in the test piece than in service, but was adopted in order to accelerate the tests. Results of tests run on steel plates with resulting lower temperatures, due to conduction, will be reported in a subsequent paper, which will also include tests conducted without the top plate (zero compression).

Accuracy of Test

The accuracy obtained with this machine has been within ±1 per cent flexure-set. A large portion of the error involved is due to the fact that no effort has been made to measure the recovered height of the sample with an accuracy greater than 1 per cent. A good idea of the accuracy can be secured from the data of Table I. If the flexure-set values of two different stocks check as close as 3 per cent, the tests

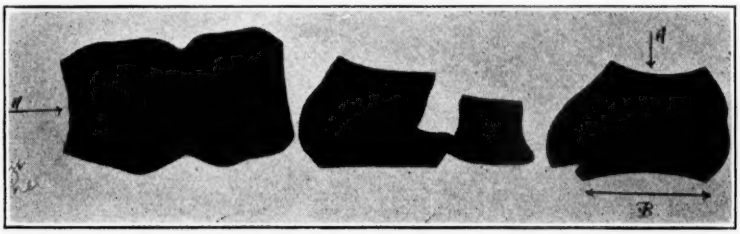
should be repeated before concluding that one stock is better than the other.

The tests recorded in Table I were made on test pieces cut from laboratory compression slabs 1.9 × 4.15 × 2.54 cm. ($^3/_4 \times 1^5/_8 \times 1$ inch). (In giving the sizes of test pieces the width, length in the direction of flexure, and height, respectively, are stated in the order named.)

Physical Results of Flexure under Compression

Examples of blow-out that occurred during flexometer tests on portions of a solid tire are shown in Figure 2. These test pieces measured 5.7 × 4.4 × 6 cm. ($2^1/_4 \times 1^3/_4 \times 2^3/_8$ inches) before the test. Failure occurred in a plane almost perpendicular to the compressive load (55.25 per cent deflection). Inspection showed a number of shorter slits parallel to the main opening. All evidence seems to indicate that failure had occurred "along the grain" produced in the process of manufacture.

Less severe tests are desirable for shock insulators and other motor products used to absorb vibration. Conse-



A—Compressive load; B—Direction of flexure

Figure 2—Examples of Blow-Out on Portions of a Solid Tire

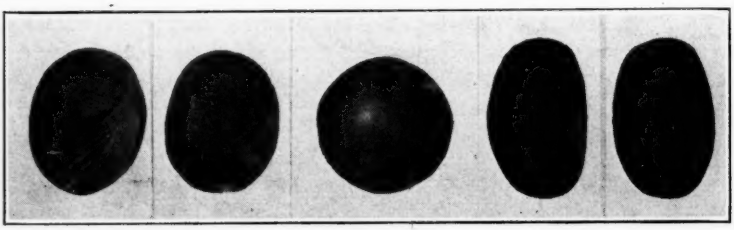
quently much smaller test pieces were used. Under a low compression (10 to 15 per cent) less flexure-set results over a period of several days than is secured at 50 per cent compression in an hour or two. The action in a stock insulator and certain types of motor supports can be simulated very well by proper choice of the load.

Under these less severe conditions of flexure there are produced several residual stresses in the test pieces in addition to sub-permanent set measured after 1-hour recovery. Such effects can be seen in the buckled appearance of the bisected test piece. Figure 3 shows a 1-inch ball before test (A), and after test (2 and 3). Sample 2 is a bisected ball of stock No. 2, and 3 is a bisected ball of stock No. 3. It is easily seen that stock No. 2 undergoes less flexure-set than does stock No. 3. Close inspection will show that the least distance across the cross section of 3 is considerably less than across a similar cross section taken farther from the center of the ball. This phenomenon was hardly noticeable in the case of stock No. 2, and is the best visual evidence of the stresses remaining after flexure has ceased.

Figure 4 shows a torque insulator (A), and a similar insulator (B) from which one arm has been cut for the test piece; also the test piece (C) before test, and flexed samples of stocks Nos. 2, 3, and 16. There are also shown the directions of flexure (YY') and of the compressive load (X). The line MN shows where the insulator is cut for the test piece. It is easily seen that stock No. 2 suffered less flexure-set than either No. 3 or 16, and also gives evidence of less residual stresses ("buckled" to a less degree).

Table II—Test Data for Different Test Pieces

Figure	Part	Size of Test Piece	Deflection (Load)	Time of Flexure
			Per cent	*Minutes*
3	Ball (for universal joint)	2.54 cm. (1 in.) diam.	50	45
4	Torque insulator	2.54 × 3.2 × 3.5 cm. (1 × 1¼ × 1⅜ in.)	54	105; stood 60 min. under load
5	Laboratory compression slab 1.9 cm. thick	1.9 × 4.15 × 2.54 cm. (¾ × 1⅝ × 1 in.)	50	120



A 3

Figure 3—Effect of Flexure of Rubber Ball

Figure 5 further illustrates the effects of flexure under compression. Stock No. 14, a so-called pure gum, showed zero flexure-set. Stock 15 showed 45 per cent. This test piece suffered blow-out, so was not bisected. Blow-out had relieved the stresses that would otherwise have remained after flexure.

Table II gives general data pertaining to the types of test pieces shown in Figures 3 to 5, inclusive.

Effect of Various Factors on Flexure-Set

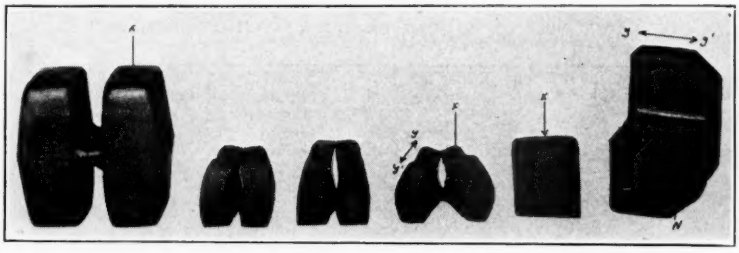
Time of Flexure—Flexure-set rapidly approaches a maximum as the test progresses. Temperature rises even more rapidly and probably influences to a considerable extent the slope of the flexure-set-time curve. This is seen by comparing curves I and II, respectively, of Figure 6. The data for the temperature-rise curve (II) were obtained on the 210-minute test (Table III). A copper-constantan thermocouple was inserted in a narrow horizontal slit near the bottom of the test piece before its assembly in the flexometer. Readings on the potentiometer were taken every few minutes for 2 hours.

The data for tests included in curve I are given in Table III. Flexure was at 55.5 per cent compression on test pieces cut from two insulators of stock No. 1, cured 70 minutes at 148° C.

Table III—Effect of Duration of Flexure

Time of Flexure	Flexure-Set	Time of Flexure	Flexure-Set
Minutes	*Per cent*	*Minutes*	*Per cent*
5	12.4	60	36.2
15	23.5	120	43.1
30	30.6	210	44.4

State of Cure—Decided undercure results in a high flexure-set. As the time of cure progresses the resistance to flexing under compression increases. Flexure-set approaches a minimum, as evidenced by the fact that overcures were found to show high flexure-set again. Curve I, Figure 7, shows that flexure-set decreases as the state of cure progresses. The tests were of 1-hour duration on test pieces from shock insulators cured 65, 70, 75, and



A 16 2 3 C B

Figure 4—Torque Insulator and Flexed Samples of Stocks Nos. 2, 3, and 16

80 minutes at 148° C. (stock No. 1) Curve II shows flexure-set resulting from 2 hours' flexure for the same cures. The 2-hour test is too severe to differentiate between the lower cures, but does show the 80-minute cure to be decidedly better than the others. Nevertheless, it has the advantage that all products showing a greater flexure-set than a "standard" adopted value based on this duration are eliminated and a high-quality product is thus assured. The data for these tests are given in Table IV. Flexure was at 55.5 per cent compression.

Table IV—Effect of Cure

Cure at 148° C.	Flexure-Set	
	1 Hour	2 Hours
Minutes	*Per cent*	*Per cent*
65	40.2	43.1
70	36.2	43.1
75	33.3	43.1
80	26.4	33.3

Hardness—Hardness is no indication of the resistance of a stock to flexure under compression, as shown by the data in Table V. Motor part 1 had been cured to the proper

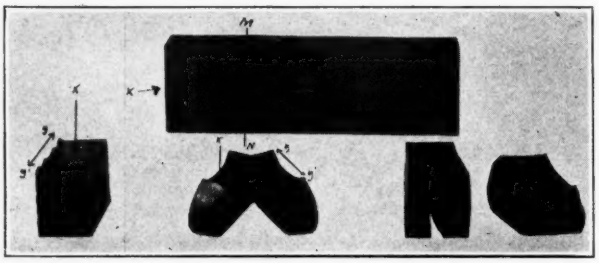
state of cure as determined by service and by flexure-set data. Motor part 2, of a different size but similar shape, was also cured to the proper hardness values. The test pieces were flexed for 2 hours under 55.5 per cent distortion. All test pieces were 1.43 × 3.8 × 2.86 cm. ($^9/_{16}$ × $1^1/_2$ × $1^1/_8$ inches). In every case motor part 2 showed excessive flexure-set. These data show the fallacy of using hardness data to indicate that cure which gives the greatest resistance to dynamic fatigue.

Table V—Effect of Hardness

Stock	Motor Part 1		Motor Part 2	
	Hardness[a]	Flexure-Set	Hardness[a]	Flexure-Set
	Unit	*Per cent*	*Unit*	*Per cent*
3	49	19.4	51	27.8
4	51	16.7	53	35.0
6	54	25.0	58	41.7
7	54	19.4	56	38.8
8	53	19.4	52	36.0
9	41	27.8	41	38.9

[a] Data by Firestone penetrometer.

Compressibility (Deflection)—Data on the deflection of a test piece of standard size by a given compressive load



14 13 11 15

Figure 5—Effect of Flexure of Laboratory Samples

fail to furnish a satisfactory indication of resistance to flexure. (Table VI) In these tests disks 1.9 cm. ($^3/_4$ inch) in diameter were cut from a slab of 0.63-cm. ($^1/_4$-inch) gage. These were then subjected to a load of 42.18 kg. per sq. cm. (600 pounds per square inch). Stock No. 4 shows the greatest resistance to flexure, yet it stands about midway in order of compressibility (column 2, Table VI). On the contrary, stock No. 7 shows the greatest deflection but stands midway in order of resistance to flexure under compression.

Static-Set and Hysteresis Loss under Compression—Permanent set under simple compression does not check with flexure-set, whereas hysteresis loss does give a quite satisfactory indication of resistance to dynamic fatigue. Some data comparing these tests are given in Table VII. Each stock is seen to stand in the same relation to the others, whether flexure-set or hysteresis data are considered. Static-set (permanent set under static compressive conditions) data are far out of line. The hysteresis values were deter-

mined by getting the load-deflection data on circular disks 1.9 cm. in diameter and 0.63 cm. thick. The maximum load was 42.18 kg. per sq. cm. The initial deflection at this load is given in column 5, Table VII. (A full report of this work together with a description of the instrument designed to study hysteresis loss and permanent-set under either constant deflection or a constant load, will be given in a subsequent paper.) Static-set tests were made on similar disks under the distortion secured by a load of 42.18 kg. per sq. cm. Tests were conducted in an oven at 82° C. for 24 hours.

Table VI—Compressibility vs. Flexure-Set

Stock	Deflection at 42.18 kg./sq. cm.	Order of Increasing Deflection	Flexure-Set	Order of Increasing Flexure-Set
	Per cent		*Per cent*	
3	21.1	4	19.4	2
4	18.5	2	16.7	1
6	19.9	3	25.0	3
7	22.7	5	19.4	2
8	20.5	3	19.4	2
9	14.0	1	27.8	4

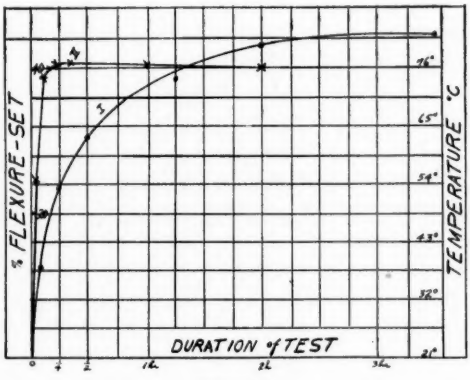


Figure 6

Table VII—Hysteresis Due to Compression vs. Flexure-Set

Stock	Static-Set	Flexure-Set	Relative Hysteresis Loss	Deflection at 42.18 kg./sq. cm.
	Per cent	*Per cent*		*Per cent*
3	14.5	30	5.85	33.7
10	14.2	21.9	4.8	37.5
11	26.0	10.0	..	51.8
12	14.8	11.0	3.95	43.0
14	8.9	0	3.00	45.0
15	..	45.0	10.55	..

Table VIII—Tensile Tests vs. Flexometer Tests

Stock	Ultimate Elongation	Stress at 400% Elongation		Ultimate Tensile		Set at Break	Flexure-Set
		Kg./ sq. cm.	*Lbs./ sq. in.*	*Kg./ sq. cm.*	*Lbs./ sq. in.*		
	Per cent					*Per cent*	*Per cent*
3	580	116	1660	217	3100	31	19.4
4	550	103	1480	166	2370	31	16.7
6	560	92	1310	140	1990	50	25
7	560	94	1340	160	2270	32	19.4
8	500	128	1830	180	2560	40	19.4

FLEXURE-SET VS. TENSILE STRESSES, ULTIMATE ELONGATION, AND SET AT BREAK—The ordinary data from tests under tension also fail to evaluate satisfactorily the resistance of stocks to flexure under compression. Comparisons of some of these data with flexure-set are given in Table VIII. It will be noted that the values for ultimate elongation are alike within experimental error (with the possible exception of stock No. 8). Set at break (the increased distance between two marks originally 1 inch apart, measured 10 minutes after the dumb-bell strip has broken) likewise fails in evaluating these stocks. Ultimate tensile likewise is of little value for this purpose. It is to be noted that stock No. 3 possesses the highest tensile (217 kg. per sq. cm.) but suffers a higher flexure set (19.4 per cent) than does stock No. 4, which has an ultimate tensile of only 166 kg. per sq. cm.

At the other extreme is stock No. 6 with the lowest ultimate tensile (140 kg. per sq. cm.), which also shows a still higher flexure-set. Similar discrepancies are to be noted in the case of moduli. Stock No. 3 with the second highest stress at 400 per cent elongation (116 kg. per sq. cm.) and stock No. 6 with the lowest stress at 400 per cent elongation both suffered greater flexure-set than stock No. 4, which possessed an intermediate value for the stress at 400 per cent elongation and also the lowest flexure-set. Table IX shows to much better advantage how poorly data of tests under tension evaluate the above stocks as to their resistance to dynamic fatigue.

Table IX—Tensile Tests vs. Flexometer Tests

Stock	Ultimate Elongation	Stress at 400% Elongation	Ultimate Tensile	Set at Break	Flexure-Set
	Per cent	*Kg./sq. cm.*	*Kg./sq. cm.*	*Per cent*	*Per cent*
10	620	95	222	37	21.9
11	650	61	200	..	10
12	619	85	188	34	11
13	480	29	65	22	37.5
15	425	155	200	25	45.0

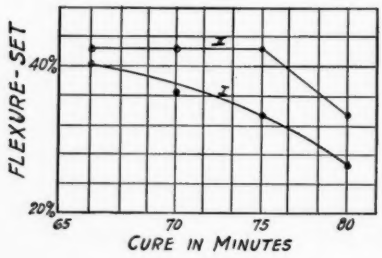


Figure 7

REPEATED-STRETCH SET—Set after repeated elongation does not help in the evaluation of stocks as to their resistance to flexure under compression. It was believed that this test, being a dynamic one, although under tension instead of compression, might properly evaluate stocks. This certainly should be the case if we believe the same as do Gottlob[3] and others.[4] The data in Table X show conclusively that set after repeated stretch under either constant load or constant dis-

[3] "Technology of Rubber," pp. 199 and 202, English ed., 1927.

[4] Davies and Norton, *India Rubber J.*, **59**, 833 (1920).

tortion does not check set resulting from repeated flexure under compression.

Table X—Set Due to Repeated Stretch vs. Flexure-Set

Stock	Set Due to Repeated Stretch: Constant load	Set Due to Repeated Stretch: Constant distortion[a]	Flexure-Set
	Per cent	*Per cent*	*Per cent*
3	20	..	20.0
10	22	15	21.9
11	22	14	10.0
12	20	20	11.0
13	[a]	[a]	37.5
15	32	[b]	45.0

[a] Broke during first elongation.
[b] Broke during second elongation.

Determination of Stretch under Constant Load—A dumb-bell test strip was stretched five times in a tensile machine at 51 cm. per sec. (20 inches per minute) to 70.3 kg. per sq. cm. (1000 pounds per square inch). The interval between extensions was only that necessary for the machine to reverse. After the fifth return the strip was removed and allowed to recover for 1 hour. Permanent set was measured as the increased distance between two marks originally 2.54 cm. (1 inch) apart.

Flexure-Set vs. Dynamometer Tests—Flexure-set results check dynamometer tests very satisfactorily.

Dynamometer Tests—Sixteen balls are assembled in a universal drive unit, each under approximately 21.65 kg. (50 pounds) compression. The alternate balls seem to carry practically the whole load of running at 1500 r. p. m. under a torque of 8.9 kg.-meters (64.5 foot-pounds). The generator shaft is at a 5-degree angle to the drive shaft. The test is stopped when the drive unit becomes loose.

It will be noted from the data in Table XI that stock No. 2 in each instance shows a greater resistance to fatigue resulting from flexure under compression than does stock No. 3. These data are typical of the results with other stocks.

Table XI—Dynamometer Test vs. Flexure-Set

Stock	Dynamometer Test: Duration	Dynamometer Test: Condition of ball	Flexure-Set: Ball for universal joint	Flexure-Set: Torque insulator	Flexure-Set: 1.9-cm. compression slabs
	Hours		*Per cent*	*Per cent*	*Per cent*
3	26[a]	High set, very poor	37.5	31.8	30
2	32¼ 38¼[b]	No set, bad	15.6	20.4	12

[a] At 3.5-degree angle of drive.
[b] At 5-degree angle of drive.

The fact that flexure-set results for stock No. 2 (or No. 3 as the case may be) do not check within themselves does not discredit the flexometer test. On the contrary, the fact that two stocks line up in the same order although tests were conducted on different volumes and shapes of test pieces as well as under different deflections and different durations of test (Table II), seems an important point in favor of the flexometer test.

Summary

Data have been presented to show that the commonly used physical tests such as stress at break, stress at 400 per cent

elongation (modulus), ultimate elongation, set at break, set after repeated stretch, and static compression-set fail to evaluate properly the resistance of vulcanized rubber to dynamic fatigue of flexure under compression, whereas flexure-set as determined in a new machine (the compression flexometer) herein described does evaluate stocks properly as determined by service and dynamometer tests. Accordingly, resistance to flexure under compression (dynamic fatigue) is suggested as a much more important property of rubber products used to absorb vibration under compression than any of the above-mentioned tests.